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EDITORIAL.

Science and Petroleum.

In his Presidential Address to the Geological section of the British Association in September last, Prof. W. S. Boulton said that it was "remarkable that British geologists should have given such little attention to the origin and occurrence of petroleum."

Before entering upon the questions which such a charge naturally raises, we must consider the nature of the evidence upon which it rests. Even the most ample publication contains but a fraction of the data present to the mental view of its author, and a vast army of observers exists whom commercial obligations restrict from publishing more than the broadest generalisations upon the information which they possess. We conclude that the passage quoted refers only to published matter, ignoring perforce that which has not yet reached publicity, and of which much is destined to pass into final oblivion. The like difference between the number of observers and of authors doubtless obtains in other departments of science where in contact with commercial interests, but the remark under consideration specially concerns geologists only.

The wording of the indictment includes two very distinct subjects, making it so broad and sweeping as to be difficult alike of direct repudiation or admission. The original formation of petroleum is a question of chemistry, biological and mineralogical, whilst its occurrence is one of geology. For one investigator into the more or less academic region of the former, there are hundreds who are devoted to the latter, of the two distinct lines of enquiry combined (or confused) in the charge with which we are dealing. Every man who is drilling for oil, whether by "wild-cat" selection of site, systematic procedure from a productive area towards its undecided margin, or scientific attack on a virgin field, is seeking knowledge as to the occurrence of petroleum. Whether possessed of geological acumen, or absolutely indifferent to anything but cash results, he is certainly interested in the occurrence of oil. There are, again, many geologists, keenly devoted to the determination of structure of oil-bearing regions, but who may be wholly indifferent to the abstruse chemical questions of its original formation.

On the other hand, the progress of organic chemistry, in both biological and mineralogical directions, tends to bring petroleum more and more into consideration, in consequence of the complexity of its composition, and to seduce chemists into speculation

as to the origin of so enigmatical a substance, and in this case the observers are of necessity of scientific habit of mind.

Experts in either science have erred widely in ignorance of the investigations effected in the other. Thus, occasionally, geologists, venturing beyond their depth in speculations involving chemical re-actions, have set forth ludicrously untenable views, whilst certain physicists devoted to polariscopic research have laid down the gratuitous assumption of rotational activity as a criterion of age, and deduced therefrom the preposterous result that the Miocene oil of Grozni is older than that of the Devonian rocks of Pennsylvania.

Whilst the origin of petroleum remains an interesting bone of contention between academicians, the questions of its occurrence, mode of storage, and best methods of extraction are those of primary importance, and we are not deeply concerned to enquire whether our own or another nation has furnished the largest number of those who are scientifically investigating these points. That there is room for many more such, to the exclusion of the unscientific "wild-cat" operator, is indubitable, and our British tendency to thoroughness should eventually give predominance (if it does not yet do so) over the most energetic push based on slipshod methods of study.

It must be remembered too, that bulk is no gauge of value in literature, and that a few pages in the present decade may outweigh, in intrinsic importance, a score of volumes of 1860–1870.

Lastly, it would be in no way remarkable that regions in which petroleum rises naturally to the surface should (after its utility became known) attract greater attention from the denizens of its places of origin than from those of countries not so favoured by Nature. The numerical preponderance of observers will necessarily depend in direct ratio upon that of the distribution of any natural substance, and matters of universal occurrence (coal and salt, for example) reckon their working investigators by thousands as against dozens in the case of rare minerals for which no practical use is yet known, although that important factor of relative significance is liable to rapid alteration of value with the progress of knowledge.

Science, cultivated in directions of practical utility, whether in individual, national or yet wider interests, affords equal, if not greater, scope for intellectual exercise with the most abstruse philosophical problems, but, to be of sound basis, must be followed in co-operation, each student conferring with those in other branches on points of mutual contact, to secure correlation of all relevant information. It is this conjunction of energies, less potent in isolation, that constitutes the chief aim of this Institution.

W. H. Dalton, *Hon. Ed.*

Sixteenth General Meeting.

A Meeting of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, on Tuesday evening, 17th October, 1916, Professor John Cadman, C.M.G., D.Sc., M.Inst.C.E. (President), occupying the Chair.

The Members of Council present were Messrs. E. H. Cunningham Craig, Arthur W. Eastlake, and T. C. Palmer, and Sir Boverton Redwood, Bart. A letter of regret for unavoidable absence was received from Mr. Andrew Campbell.

The Hon. Secretary (Mr. Arthur W. Eastlake) announced that the following gentlemen had been elected :—

As *Members* :—William John A. Butterfield, Herbert James Davies, Arthur William Ibbett, Frank Mortimer Penny and Louis C. Sands. As *Associate Members* :—Stanley Edward Bowrey, Bernard J. Ellis, and Roderick Harry Parnell. As *Students* :—Hugh Peter W. Giffard, Alfred Ulrich Max Schlaepfer and William Rupert Weatherhead.

The following paper was then read :—

The Norfolk Oil-Shales.

By William Forbes-Leslie, M.B., F.G.S., *Member*.

The paper I have the honour to read to you this evening is largely a record of facts in regard to research work upon the Norfolk portion of the Kimmeridge outcrop. I am aware that the paper contains many shortcomings, but in view of the importance of the subject, I am impressed to seek the kind indulgence of my hearers in its presentation.

I am greatly indebted to your late President, Sir Boverton Redwood, for much valuable advice and assistance, without which the present stage of development could not have resulted.

To Mr. John Wells belongs the credit of demonstrating the commercial value of the shales, in superintending distillation in the field, and determining the quantity and quality of the oil contents.

The Coalfields of England have been the true foundation of England's economic life. Upon that sure basis of power the energy of her national life has been established. The riches of the world have been sent to her to be transmuted into more precious riches. And the growth of her wealth and the establishment of her Empire have been assured from the same source by the gift of a kind and beneficent Nature.

But times change, and in their passage are evolved new conditions which require the modification of methods in the arts and manufactures. The mighty push forward which men call progress, affecting mind and matter, demands likewise change in economic conditions as a direct result of mental and physical advancement.

And in no age of the world's history, as far as written history can be the judge of past civilisations, is this onward push so evident in the world's economic life as it is to-day. The progress from a primitive beginning has been long and wearisome, and centuries have been required to advance humanity one step along the road of evolution, but in these days, evolution rushes along on fiery wheels, making men marvel sometimes, whether having successively conquered the earth, the ocean, and the air, they shall not finally mount a ladder of their own making to a superior world.

The world has passed many sign-posts in this Pilgrim's Progress, and age after age man turns to advantage more and more the natural products of the earth and its surrounding media, being forced thereto by the gaunt form of Necessity, the instrument of evolution. And to-day humanity has reached another sign-post. It stands mid-way on the line of separation, between the Coal Age which is passing and an Oil Age which has come, and in which may be dimly discerned a main factor of the future economic life of humanity. So rapidly has the change been effected that men have not yet fully grasped the mighty revolution. They are prone to think that oil as a source of energy and power is an ephemeral factor in the world's economy, one whose influence does not strike deep enough to be permanent, and that in comparison to the Coal Age, the Oil Age is in point of duration a passing episode.

As an architect maps out the streets of a city, so are engineers able to measure the width and depth of the world's oil areas, and to say, "Here is our oil wealth, here the source of our energy and power in the future," and to calculate the balance between supply and demand, and the distance of the period when the oil supplies of the world shall be exhausted. How often have the like calculations been made with regard to the world's coal supplies! But year by year, decade by decade, further coal fields are discovered, to refute the belief that man has compassed the height and breadth of the potentialities of Nature, or with his finite measuring line grasped the infinity of her resources.

And with regard to oil it is the same; there are those who declare that the oil supplies of the world are nearing exhaustion, and that mankind will return to the more substantial, though less concentrated, form of fuel, which lies included in coal seams. But this

doctrine was preached when the Pennsylvanian oil-fields were the great source of oil in the world. And since then there have been discovered the Russian, the Rumanian, the Persian, the Californian, the Mexican and others; yet the surface of the crust is only scratched, and there is space enough, and rocks enough, to comprehend infinitely vaster oil-fields than at present supply the world's demand for oil. Yes, and terrestrial history comprises periods enough, and conditions suitable, to fill these spaces with great deposits of oil. Nor do we know that in a moving world of effects, the causes of which are beyond our perception, the manufacture of oil is not proceeding more rapidly than its exhaustion by human means; or that from the deeper sources the substance will not in time migrate to the more superficial parts of the crust, to be discovered and tapped by man for the supply of power and energy to a newer and more highly organised civilisation.

Whether it be believed or not, whether it can be realised or not, the truth is the same: the life of man on this globe, his future progress and economic advancement depends on concentrated forms of energy and power. These lie embodied in liquid fuels, and in those processes which shall utilise the maximum energy of the substance, with a due regard to the retention and elaboration of valuable by-products. Nor is it possible to believe that coal itself will long remain a fuel in the present sense of the word, or that more economic methods will not be elaborated to transform its power into more concentrated forms which will permit the utilisation of its numerous by-products.

It is a sensible principle of scientific study which draws attention to the economical methods of exploitation, which should be adopted in the utilisation of liquid fuels, and to the available balance between supply and demand at any given date in the history of the mineral, but it throws an anticipatory gloom of tragedy, almost of terrestrial catastrophe, upon human life to assign a termination to the reign of any one predominant source of energy in nature, without the substitution of a better. It clouds the sphere of reason in human genius, and prepares man for the frustration of all his efforts. It applies the drag, but not the incentive to man's mental progress.

For once on the long road of human progress from darkness to light, from antiquated and worn-out conservatism to modern efficiency, the inventive genius of man has worked in co-operation with a beneficent Nature, so that when the Oil Age arrived, human intelligence was able to grasp its mighty possibilities, and to turn them to account through the discovery of the internal-combustion engine, and other mechanical contrivances.

These two factors interlock. And through the archway thus formed humanity has already passed into a new age, the vast possibilities of which are only dimly comprehended by the present civilisation.

From the earliest times reference has been made to the natural product which under the various names of Petroleum, Mineral Oil, Rangoon Oil, Earth Oil, Bitumen Oil, Persian Naphtha, &c., has been known to the ancients, our immediate forefathers, and which has frequently been mentioned by writers of antiquity and later authorities. The records of China and Japan afford additional evidence of its occurrence in the form of gas, which has been used for illuminating purposes, for a period long anterior to the Christian Era. But in all these historical references the fact remains unquestioned that Western Asia supplies the earliest knowledge of the subject, and that it is only in Roman and later times that reference has been made to petroleum in Eastern Asia, Europe and America.

It remained for America to first demonstrate the presence of vast quantities of free oil in rocks below the surface, and its economic advantages as an illuminant, together with its use in the generation of mechanical power.

Its value has caused research to be made in almost every part of the habitable globe, with the result that the ancient sources of Western Asia have already yielded enormous quantities of oil, and lands where there was no suspicion of oil existing at all, have now added, if anything, greater volumes of the product to the requirements of man.

Oil occurs in nature in three fundamental forms:—

(*a*) Free liquid oil, or petroleum.
(*b*) Natural gas or casing-head gas.
(*c*) Shale oil, or kerogen oil.

Shales, however, may contain crude petroleum or bitumen, and these are equally entitled to be called oil-shales. Almost every coal, more especially cannel coal and coking coal, yields petroleum on distillation. They do not yield it by treatment with solvents. It may be said, therefore, that they contain kerogen. Again, there may be, in the same shale, both free oil and kerogen, free oil in one case being greatly in excess of kerogen oil.

In Britain sources of oil may be divided into oil derived from shale by distillation, oil derived from coal by distillation, and oil derived from subterranean sources, which in several instances have been proved to resemble a true petroleum.

These general remarks will be sufficient to punctuate the importance of the subject in its wider sense, and lead to a specific review of its bearing upon sources of oil in the United Kingdom.

Historical Aspect.

The treatment of this topic falls naturally into two divisions, respectively dealing with English oil-shale and Scotch oil-shale.

English Oil-shale.—In England, oil is derived from kerogen shale, bituminous shale, and shales containing both kerogen and free oil, situated in strata belonging to the Jurassic and Carboniferous systems. The first historical reference to oil-bearing shales is to those of Kimmeridge, in Dorset, mentioned in the Parliamentary Statutes of Queen Elizabeth, but proof is not wanting that the shales were worked in Phœnician times, apparently not for the oil they contain, but for some peculiar property which the ancients prized, and which is still a mystery to present-day antiquarians.

Since Queen Elizabeth's day, the shales of Kimmeridge have been sporadically worked from time to time, but without any measure of success. More than fifty years ago, a company was formed to manufacture naphtha, paraffin grease, petrol varnish, paint and ammonia. Another company was formed at Alston with the ostensible object of manufacturing mineral oil. It was liquidated in 1872. Another was formed in 1876. It had for its object the introduction of carbonaceous residues left on the destructive distillation of the shale as a substitute for coal charcoal. All these companies were unsuccessful.

The reason for the failures cited above was not so much from any cause in the shale itself, saving perhaps the sulphur-compounds, but rather that the proper methods had not been invented to utilise the oils and the by-products (which are now found so valuable in the case of the Scottish oil-shales), and that the machinery of the period was not suitable for the proper combustion of oil fuels. All these attempts to work the English shale-oil fields were premature.

Dealing first with the Carboniferous system, we find in several coal-fields of this country intercalated bituminous shales which on distillation yield oil. Many of the instances, however, brought to light by practical miners, fall within another category of oil origins, namely, seepages of free oil or petroleum, rising from unknown sources in pre-Carboniferous rocks. Still there are, undoubtedly, oil-shales of the Carboniferous system, especially in the county of Flint, which have yielded considerable tonnages for

treatment. But as far as visible computation of their reserves can be made, they are entirely overshadowed in importance by the oil-shale of the Upper Jurassic horizons.

Scotch Oil-shale.—In Scotland the treatment of bituminous and kerogen shales as a source of oil was first undertaken by Dr. James Young of Renfrewshire, to whom, therefore, the Scottish oil-shale industry owes its existence. The credit, however, of having first discovered and investigated the properties of solid paraffin (produced from wood tar) belongs to Reichenbach, who was able to demonstrate such properties as early as 1830; whilst the presence of paraffin in petroleum was recognised some time anterior to Reichenbach's discovery. Fuchs and Buchner, in 1809 and 1819 respectively, separated solid hydrocarbons from Tegernsee oils, and in 1835 Von Kobell identified them as paraffin.

It was in France, however, where the first economic exploitation of so-called bituminous shale took place. In 1830 Laurent obtained paraffin by distillation of such shale, and in 1835, he suggested the treatment of Autun shale with a view of manufacturing the products obtained from it on a commercial basis.

The credit of placing the shale industry on a really commercial basis is due to Selligue, who was able to perfect the distilling process, and then purify the distillate, thereby enabling paraffin to be produced under economic conditions. This was accomplished prior to 1845.

In Scotland it was not till 1847 that Dr. James Young, who was Manager of a Chemical Works at Liverpool, had his attention directed by Dr. Lyon Playfair to a source of oil at Alfreton, Derbyshire.

The oil flowed in a small stream from the top of a coal-working at Riddings pit. Young succeeded in extracting from this oil three important constituents on a commercial scale, namely, light burning oil, heavy lubricating oil and paraffin wax.

This source of oil, however, was soon exhausted, and Young transferred his efforts to the treatment of coal. He endeavoured to imitate the processes of Nature by which he erroneously believed the oil to have been produced. The coal was exposed to the action of a gentle heat, and in 1850, Young made his process the subject of a patent.

In the course of Young's experiments, a highly bituminous mineral was found called Boghead coal or Torbanite, and Young confined himself to the commercial exploitation of this substance.

In 1862, Young's source of supply was again exhausted, the Boghead coal being worked out, and henceforth the Scotch oil-

shale industry has had to depend entirely for its supplies on the bituminous or kerogen shales of the coal measures, which were first worked at Broxburn by Robert Bell in 1862.

Geographical Situation of Oil-shale Fields of the United Kingdom.

English Shale-fields.—The geographical situation of the oil-shale series of the Jurassic system in England comprehends a large portion of the southern parts of this country. Its outcrop is found included in the counties of Dorset, Somerset, Wilts, Gloucestershire, Berks, Oxfordshire, Buckinghamshire, Bedfordshire, Cambridge, Norfolk, Lincolnshire, and Yorkshire. The exposures of the series form a long sinuous line following the shore of the Upper Jurassic Sea. In Norfolk the series is flexured, a spur of the outcrop passing northward under the Wash, while the main line runs northwest through Lincolnshire, to reappear from beneath the Cretaceous overlap on the north side of the Yorkshire Chalk wolds, passing with eastward strike into the North Sea.

The oil-shale series of the Carboniferous system is an integral part of the coal basins of England. Considerable investigation is required, however, before it is possible to define the extent of area underlaid by them, or to demonstrate the number and thickness of the seams and their stratigraphical relationship. Their importance has in every case been overshadowed by the coal seams and measures of which they form part, and in many cases it is only due to there being an obstacle to safe mining of the coal that we have heard anything about the shales themselves.

Scotch Shale-fields.—The geographical situation of the Scotch subdivision is included in an area which is located in the centre of Scotland. The productive portion of this is covered by West Calder, Uphall, Queen's Ferry, Loanhead, and Burntisland. Briefly, the oil-shales appear to have been laid down in subsidiary basins, occupying the counties of Linlithgow, Edinburgh and Peebles.

Geology of the English Shale-fields.

In England no bituminous or kerogen shales of economic value have been encountered in rocks younger than the Jurassic. The Eocene, Oligocene, Miocene and Pliocene divisions of the Tertiary have been in many places exposed by natural erosion or the drill. No indication of mineral oils have been observed in their members. Other countries such as Russia and Rumania have supplied enormous quantities of liquid petroleum from Tertiary strata, and

in Peru oil-shales occur in rocks of Tertiary age. Whatever be the cause, the fact remains that oil and bituminous shale are both absent from the Cenozoic rocks of Britain.

Similarly the Cretaceous series exhibits no bituminous shales, although the remains of plants and animals are preserved in abundance throughout several horizons, and even thin coal seams are exposed in some localities.

The third division of the Jurassic succession in England, or the Kimmeridge clays, so-called from the place where it was first studied, covers extensive areas in the south and east of England, extending from Dorset on the south-west to the Wash, in a broad continuous band, varying in width, as it is approached by the younger Cretaceous or Tertiary rocks, or as these recede from it. It is sometimes overlain by the second division or the Portland beds, of its own system, but at times these and the first division or the Purbeck beds, are eroded, or absent through default in deposition, and the exposed Kimmeridge clays are covered unconformably by Cretaceous, Tertiary or recent beds.

The whole length of the Kimmeridge outcrop from Dorset to Lincolnshire is indented in such a manner as to suggest depressions of more or less lenticular form; and although later movements, having their genesis in inter-Jurassic, inter- or post-Cretaceous times, have affected the form of these, or in places even reversed their original axes of deposition, there are still evidences available, despite these flexures, the irregularity of deposit in the succeeding geological ages, and the several erosions affecting the Kimmeridge beds since their first accumulation, to demonstrate the conditions of their deposition, and to some extent their limits, whether exposed or concealed beneath the younger rocks.

The chief historical example of an oil-shale area on the outcrop is that of Kimmeridge in Dorset, on the extreme south-west of the Kimmeridge line, where a lenticular depression is demonstrable, partly exposed and partly concealed beneath Cretaceous rocks, although not in every case beyond a workable depth.

At the great deflection of the outcrop in West Norfolk, there has been lately investigated another lenticular depression or basin, partly exposed, and partly concealed beneath a thin cover of younger rocks, the centre of which is believed to be at, or near, the village of Wormegay, in Norfolk.

Between these two points, there are indications of other Kimmeridge basins, both visible and concealed, in the long and sometimes wide belt of Upper Oolite rocks, close investigation of which might probably disclose included bituminous or kerogen-bearing shales.

Oil-shale basins of the Kimmeridge Measures. 1. Concealed basins.—Presumptive evidence of the existence of at least two basins of the Kimmeridge measures has been detected by the drill. For the purpose of this paper, they may be called the Wealden oil-shale basin, and the Essex-Kent oil-shale basin.

The Wealden Oil-shale basin is situated in the county of Sussex, and lies deep under a discordant sheet of Chalk, Wealden and Purbeck-Portland beds. It connects with the Kent oil-shale basin across the Crossness-Brabourne line, along which a series of boreholes have demonstrated underlying Silurian rocks. Six boreholes have revealed its presence. One at Dover proved 44 ft. of Kimmeridge clay, containing horizons of bituminous shales. Another at Elham, proved 108 ft. without penetrating the beds. Another at Brabourne gave 262 ft. of Kimmeridge clay, while one at Battle passed through 1,273 ft. of Kimmeridge clay, containing apparently rich bituminous shale. A boring at Penshurst, near Tunbridge, proved 622 ft. without piercing the Kimmeridge series, while at Pluckley, further east, 526 ft. of Kimmeridge beds were encountered without passing through them.

The point at which the Kimmeridge beds were met with nearest the surface was at Battle, where the top of the division was only 292 ft. down. At Brabourne they were 710 ft., at Elham 707 ft., and at Dover 457 ft. from surface. But at Penshurst they lay deeper, at 1,245 ft., and at Pluckley, 1,261 ft. from surface.

It is difficult to determine the size of the Wealden oil-shale basin, owing to its concealment under younger beds, and also from the tectonic effect of the rise of the Wealden anticline.

Its eastern and northern limits are more or less revealed by the boreholes already quoted, but its western and north-western boundary have still to be defined. The presence of natural gas at Heathfield is a point of considerable significance, not only in demonstrating the presence of gas, stored in the Purbeck beds, but in the probability of this gas having its origin in a natural distillation of the Kimmeridge shales in the thickness of the Wealden anticline.

The Essex-Kent Oil-shale basin probably covers the greater part of the counties of Cambridge, Essex and Kent, and for convenience in grouping is divisible, geographically, although apparently not geologically, into a southern basin, the Kent Oil-shale Basin, and a northern one called the Saffron Walden Oil-shale Basin.

Kent Oil-shale basin.—The existence of an oil-shale basin in Kent is revealed by borings at Dover, Elham and Brabourne, where Kimmeridge clay containing bituminous seams was found in

its correct stratigraphical position, but also exhibiting signs of erosion and default in deposition. These fragments of a great period are capable of a correct correlation with the main body of the series farther west and north at Pensburst, Pluckley and Battle. Although the borings along the Brabourne-Crossness line, but east of it, within the Kent coal basin, have not, with the exception of the two borings already mentioned at Elham and Dover, revealed the existence of Kimmeridge beds, they have undoubtedly demonstrated a series of great, and, apparently, prolonged periods of denudation which satisfactorily account for the absence of the Kimmeridge clays, and the Battle borings show that as the geosynclinal axis of the Wealden basin is approached the Kimmeridge clays exist in normal sequence of position overlying the Coralline beds.

A connection between the Wealden basin and the Kent basin is certainly effected immediately south-east of Brabourne, by way of Elham and Dover. Connection with the Saffron Walden basin may exist under the estuary of the Thames, and east of the London Palæozoic platform.

The Saffron Walden Oil-shale basin includes the greater part of the counties of Cambridge and Essex, and portions of Hertfordshire and Suffolk. The position of the Kimmeridge clays in this area is confined to, and forms part of, the contents of a wide interval situated between the eastern edge of the London Palæozoic platform and the presumed western edge of a range of very ancient Palæozoic rocks, directed approximately northwest—southeast, or more or less parallel with the folds of the Charnian axis.

The Kimmeridge series comes to the surface in the Cambridgeshire section, but as its course is followed south-eastwards, Chalk and Tertiary beds are brought over the Kimmeridge, till the top of the series, if present, is buried 400 to 1,400 feet deep.

In the Saffron Walden boring no record is given of any included bituminous shale seams, but it seems improbable that, where the conditions subserving their establishment are proved to exist to the south in the Kent Wealden basin, and to the north of them in the Norfolk basin, they should be absent in the Essex portion.

2. *Exposed basins.*—Only two oil-shale basins of the Kimmeridge outcrop have been the subject of scientific investigation, the Kimmeridge-Portisham basin in the county of Dorset, and the Wormegay basin in the county of Norfolk.

The Kimmeridge-Portisham Oil-shale basin is situated in Dorsetshire, upon the extreme south-western end of the Kimmeridge outcrop and has been so often described, and so long known, that it

requires no further description. So historical is it that the village of Kimmeridge itself has given its name to the third division of the Jurassic system.

The Wormegay Oil-shale basin differs historically from the former in being comparatively little known. It is a new discovery, the facts of which, resulting from recent investigations, have not, as yet, been made public. It is the specific object of this paper to enumerate such of these as at present can be made known. The extent of the basin is not yet sufficiently determined to enable a correct definition of its boundaries. It seems to follow specific geological feature lines, the origin and position of which will be dealt with in a subsequent paper.

Topography of the Wormegay district.—The surface of the county of Norfolk included within the limits of the Wormegay oil-shale basin is, in general, flat and uninteresting, especially so in the north-western and central portion, where it approaches the border of the Wash. Fragments of Greensand appear on the surface of the Kimmeridge clays as outliers, which in places confer a ridged and irregular contour upon the surrounding country. On the eastern edge of the basin, however, the outcrop of the Lower Chalk forms a prominent landmark, while, if closely scrutinised, evidence of ridges quite apart from those forming the outcrops of the younger periods, or the remains of their erosion, may be discerned; the ridges running parallel and having a suspicious general relationship with the rivers Nar, Wissey and Little Ouse.

Geology of the Wormegay basin.—The surface of the basin is found to be covered with deep soil, beds of blown and recent sands, brick- and boulder-clays and gravel. Many of the small ridges are composed almost wholly of moraine material with a foundation of Greensand which they have helped both to erode and to conserve. But in almost every case, the natural valleys have been deepened or gouged out by glacial action, the higher ground being composed of moraine detritus. Erratics are common, composed of granites, quartzites, limestones and various igneous rocks. The rocks forming the floor of the basin, which support these remains of Glacial and recent conditions, belong to the third division of the Jurassic. They are composed of clay, shales, sandstones and limestones; in some cases these beds are highly fossiliferous, and much trenched by inter-Cretaceous and pre-Glacial water-channels, containing the remains of a great erosion of the Chalk and Greensand. In other places Greensand is found in position, occupying depressions or ancient riverine channels in the Kimmeridge clays which must have resulted from the elevation of this area in pre-Cretaceous

times, probably during the period when the Purbeck and Portlandian stages were being laid down in other parts of England.

This trenching has affected, not only the upper series of blue clays and shale, but also beds of ancient alluvium, representing the land surfaces of Upper Oolite times.

Towards the eastern edge of the basin, the Lower Greensand and Gault, Upper Greensand and Lower Chalk successively form the overlie of the Kimmeridge clays. At Holkham as much as 748 feet of Chalk and Greensand are interposed between the surface and the top of the Kimmeridge series.

The visible or shallow stratigraphical horizons of the Wormegay basin comprise the Cretaceous rocks from the Lower Greensand eastwards to the top of the Lower Chalk, the Wealden and Hastings beds being absent in these localities, and westwards the Upper Oolites, with the exception of the Purbeck-Portlandian substages, which do not appear to have been laid down in the east of England.

Tectonic conditions of the Wormegay district.—The visible features of the Wormegay oil-shale basin are much masked by recent geological events, especially those which have been responsible for the recession of the Wash in historical times. It is evident that during Tertiary or, more certainly, during Cretaceous times the district had formed a distinct land mass of considerable height above sea-level which was much eroded by aerial action and trenched deeply by inter-Cretaceous, Tertiary and pre-Glacial water channels, for we find under the Glacial drift the remains of river beds, deeply cut into the Kimmeridge clays, and containing a great erosion of the Lower and Upper Chalk and Greensand, with large water-worn fragments of Puny Drain oil-shale.

The glacial detritus is deposited on the flanks of ridges, and it is evident that the glaciers themselves have followed the course of ancient valleys of pre-Glacial origin, gouging them more deeply and depositing moraine material on the adjoining slopes, which at present in a great measure masks their original configuration.

The greater valleys of the district, most of them still riverine in character, exhibit considerable thicknesses of boulder clay lying upon Kimmeridge beds. But in no case has glacial action done more than trench the overlying clays of the oil-shale series.

The latter, in all cases where examination has been possible, are found intact.

These river valleys, such as the Nar, the Wissey, the Ouse and the Little Ouse, with their respective watersheds, form the principal feature-lines of the basin. Along the course of the River

Ouse, the Kimmeridge beds are brought up to the surface, and where visible, are observed to dip east at an angle of about 7° beneath the younger series. The opposite direction of dip is observed farther south in Cambridgeshire on the same line of strike. On the northern end of the line there is positive evidence of a western dip in the series, but at a steeper inclination than on the east. It has been determined by accurate measurement in shaft sinkings, that the dip to the west is as much as 1 in 5, or 20°.

The strike of these exposed beds can be traced for over 8 miles, and in all this length the included oil-shale series is found intact in its true stratigraphical sequence.

Farther east on the dip, shafts, borings and fieldwork have demonstrated that secondary folds are responsible for bringing up to, or near, the surface the same series of Jurassic beds beneath a thin cover of younger rocks.

The principal visible fold of the basin is, therefore, the Ouse Valley fold.

At right angles to this are apparently parallel folds more or less in alignment with the Nar, the Wissey and the Little Ouse. These are not easily distinguishable, owing to their being masked by moraine gravels and clays. It seems possible from present evidence, however, that the above rivers and their watersheds comprehend a north-west and south-east series of foldings at a wide angle from the north and south foldings of the Ouse Valley. It is probable that the riverine valleys occupy the crown of submerged ancient folds and their watersheds are the remains of ancient trough folds. The Nar Valley is almost certainly a ridge fold of pre-Cretaceous time. Where it meets the line of the Ouse Valley outcrop, subsidiary foldings occur in the latter at right angles. There is further evidence available of a N.W.-S.E. system of folds which would necessarily form a sectional arrangement of the basin.

Indeed, it may be demonstrated hypothetically that the Wormegay basin is a part of a much larger depression having its western boundary along the Ouse, its southern lip along the Culford pre-Palæozoic fold, its northern concealed edge below the Chalk at Holkham, and its eastern hidden extension west of the Tertiary outcrop.

In none of the movements which have been responsible for the changed form, or sectional arrangement of the Wormegay basin, has there been such intensive action as to fault or denude the Oil-shale Series from their original seat of deposition. Nor have the inter-oolite movements, as far as observed, caused default of such deposition in any area within the basin.

The beds themselves do not exhibit those lithological characters common to areas affected by metamorphism. In this they differ from the western facies of the same series in Dorset.

Investigations in Wormegay basin.—Where denudation has exposed the Kimmeridge clays in the Wormegay basin, evidence of oil-shales being intercalated in these clays has, from time to time, been demonstrated. Fragments of highly productive shales have been found on the surface, or discovered in trenching or draining operations, and these have excited local interest through the power they possess of burning brilliantly when thrown into the fire.

Selwyn, however, appears to have been the first to observe that oil-shale existed in Norfolk, and the result of his examination is stated to have been the discovery of a large body of rich bituminous shale.

It was not, however, until just previous to the beginning of the War, that any research work of a specific nature was undertaken upon the Norfolk end of the long Kimmeridge outcrop. The investigation revealed the presence of an oil-shale series of very considerable importance.

Stratigraphical sequence of the oil-shale series.—In section, the oil-shale series, where exposed in the Puny Drain, immediately east of the Ouse River at Setchey in Norfolk, consists of alluvium, recent sands, peat, boulder-clay and boulder-gravel, varied by Pliocene sands and the buried detritus of inter-Cretaceous time underlaid by black-blue clays belonging to the Upper Kimmeridge beds, which are much trenched by pre-Glacial drainage channels, containing the remains of a great erosion of the Chalk and Greensand.

This trenching has affected the upper series of blue clay, but in no place has it apparently been responsible for the absence of the oil-shale series. These latter, wherever they have been encountered, are found intact beneath the pre-Glacial water-channels.

Lithologically, the clays are sharply divided from the included oil-shales. It is possible to distinguish two types of oil-shales occupying the upper horizons of the Kimmeridge clays on the northern section of the Ouse Valley outcrop.

The highest in the series consists of dark brown bituminous-looking shale, included in dark blue clays, and capped by limestone. There are several stages from above downwards wherein it is possible to distinguish a gradual differentiation in the structure of the shales, by which they become more porous in texture and lighter in colour. Towards the base of this series yellow sandstones are encountered, exhibiting quantities of bitumen between their bedding planes. The second class of shales lies beneath the

former without any visible unconformability, the dividing line apparently being the sandstone stage already described. The oil-shales are more open in texture, bluish in colour, and contain vast quantities of marine fossils, together with quantities of fish remains. The fossils are very much larger than those in the upper series. The including clays are greyish-blue to black-blue in colour, and there is evidence of one or more land-surfaces throughout the series. For convenience in classification the upper series has been called Smith's from the farm on which it is found, and the lower has received the name of Puny Drain series from the Puny Drain, where the outcrop was first discovered.

Palæontological evidence of position.—The visible outcropping beds in the Ouse Valley along the Puny Drain are undoubtedly the result of late Jurassic sedimentation. The Geological Survey groups all the ground between the edge of the Lower Greensand westwards to the Ouse River as Kimmeridge, but does not, as far as known, divide the exposures into the several horizons of Kimmeridge time. The irregular sequences which are observed at March, Soham Mere, Southey and Denver, and along the crown of the Ouse Valley outcrop, as well as those deeper and wider zones of movement common to the east coast, reasonably lead to a conclusion that there has been diverse, although related, movement expressing itself in an arcuate arrangement of folds within the basin itself, and generally affecting, as post-Jurassic modification, the level of the Kimmeridge sediment.

Palæontological evidence is valuable in helping to distinguish the various horizons in sedimentation existing in the English Kimmeridge. At March, the Survey describes *Ammonites biplex*, a fossil of Upper Kimmeridge time, as common in the Kimmeridge beds, and *Amm. cordatus*, which being a Coralline Ammonite may have been washed from Coralline beds when the Upper Kimmeridge was being laid down at March. At Denver, Coralline Ammonites have been discovered in what appears to be Kimmeridge beds. At Soham Mere, Coralline limestone is exposed. On the Ouse Valley outcrop, the highest bed of any stratigraphical importance as a datum level, is a thin limestone filled with types of *Ostrea*, fish-remains, and small Ammonites of the *biplex* variety. Above this limestone no oil-shale beds have so far been discovered, and it may be taken for all practical purposes as a datum line, especially in the northern section of the outcrop, marking the top of the series.

Beneath this limestone, the first beds of Smith's series were discovered. The shale is very dark in colour, and is prone to split in thin sheets along the bedding-planes, although there is evidence

of fracture-planes, the result being an angular shape conferred upon fragments when broken. The fossils are small in size, and in this respect differ decidedly from the lower series. The Ammonites are principally of the *biplex* variety, while there are small types of *Ostrea* and *Lucina minuscula* (Blake), and fish-remains.

The Puny Drain series differs from the above in not containing any yellow sandstones with bituminous coating. They appear as bluish-grey beds, very porous in structure and containing large quantities of marine fauna. So prolific are they in this respect, in individuals, although not in genera, that the rock appears to be covered with white spots. These are largely composed of *Lucina minuscula* (Blake), *Orbiculoidea latissima* (J. Sow.), and large specimens of degenerate Perisphinctoid Ammonites, large types of *Ostrea* (sp.) and numerous fish-remains.

These members of a marine fauna are sufficient to demonstrate the position of the Kimmeridge clays in the Wormegay basin. They appear to belong to undoubtedly Upper Kimmeridge time.

Productive Oil-shale divisions.—Two productive divisions of the series are known, and have been described already in the palæontological section of this paper. The first is called Smith's Series, from the name of the farm upon which they were first struck. Beneath occur the Puny Drain clays and shales called after the Puny Drain, where the outcrop was first exposed. The thickness of Smith's division may be anything from 100 to 300 feet, and undoubtedly comprehends several rich oil-shale seams. Two have already been discovered, one under the limestone capping, and the second and larger seam immediately overlying the sandstone stage, which is believed to be more or less the divisional plane between Smith's Series and the Puny Drain Series. The seam cut in the lower part of Smith's Series is not less than 6 feet thick, and contains as much as 50 gallons of oil to the ton.

The next division underlying the former has been called the Puny Drain Series. It undoubtedly includes one or more rich oil-shale seams. One of these has been exposed in the banks and bed of the Puny Drain, south of King's Lynn. This seam is of a bluish-grey colour, open texture, and when newly broken into, is found to exude free oil. This is especially the case when the broken out fragment is subjected to running water, as originally demonstrated by Mr. John Wells.

A similar instance of free oil being confined in the shales is found when the limestone capping of Smith's Series is broken through. Water covered with oil immediately rushes into the workings.

The including clay beds are slate-blue in colour, and do not

show any apparent trace of oil. The thickness of this seam is not less than 7 feet, and on distillation it yields from 50 to 51 gallons of oil per ton.

It is probable that the thickness of the Puny Drain Series is not less than 200 feet, and it may be as much as 500 feet. The bottom of the clays has not yet been determined.

The aggregate thickness of the shale seams already proved to the east of the outcrop, which are capable of economical development, is 13 feet, but other evidence is available which renders it probable that several other seams will be capable of exploitation.

Physical characters of the Oil-shales.—The physical characters may be considered under macroscopic, microscopic and chemical composition.

Macroscopically, the shale appears to be of two kinds: The Upper Series or Smith's Shale is a rather close-grained rock, dark brown in colour, splitting along the bedding-planes into thin laminæ, but with distinct planes of fracture. The shale is highly elastic. When exposed to air and sunlight, it rapidly loses moisture, and becomes light in weight, but none the less durable. Fragments of this class of shale are often met with on the grass lands of the district.

The underlying or Puny Drain Shale may stand as a general type of all the shale series below it. It is a greyish-blue rock, less apt to split along its bedding-planes into thin laminæ, but prone to break into thick and wide plates along fracture planes, and thus resembles certain sandstones. No cross-bedding has so far been observed in it. The surface of the planes is covered with a vast assemblage of calcareous fossils, many of them impinging through the plane upon which they have fallen, and resting upon lower planes. If viewed edgeways, after fracture, across the bedding-planes, the rock is observed to be roughly vesicular or open in texture, resembling somewhat certain types of pumice. It differs from fragments of the Dorset-Blackstone seam in its colour, and especially in the shape of the fragments. On drying in the air, the rock becomes light in weight, and on percussion gives a note something like that of wood.

Under a magnifying glass, Smith's Shales exhibit porous structure on vertical section. The body of the substance is dark brown to almost pitch black, but on cross-section it has a greyish-green colour. The porosity of the shale is parallel to the plane of the bedding, the laminæ having some porosity, besides that given by the planes of stratification. The body of the shale is filled with calcareous fossils, or fragments of such. They mostly lie along the bedding-planes, but on cross-section may be observed

to disturb them. The smaller fossils are much flattened, although in the larger specimens, the casts are outlined according to the form of the organism, and have escaped flattening.

In the Puny Drain Series the magnifying glass shows the shale to be of still more open texture. In this case, likewise, the porosity lies along and comprehends the bedding-planes. The colour of the matrix is a bluish-grey, changing here and there to a green tint. The open texture of these shales is remarkable, and their absorbent power must be very great. In appearance, under macroscopic examination, they are more or less vesicular.

A number of slides have been prepared from Puny Drain Shale. The specimens exhibit many interesting characters. In vertical sections under a high power, the field shows numerous straight lines, representing the bedding-planes. These are more clearly indicated by strings or lines of carbonaceous material, which, however, have the peculiarity of wedging out on approaching one another. Numerous rounded spaces occupy portions of the field, resting upon the bedding-planes, but also appearing irrespective of them. They resemble the mouths of loculi, filled with organic material of a somewhat lighter colour than the carbonaceous matter of the wedges. That their contents are organic, and not inorganic, material is proved by their optical character.

With the exception of the above two classes of material, practically the entire field of the specimens is uniformly composed of a yellowish resinous-looking substance which may possibly be a form of kerogen.

When a higher power is used, it is seen that this yellowish resinous-looking content is composed of two distinct substances. A distinction is drawn from differences noticeable in their colour, in their refractive indexes, in their optical outlines, and in their visible and material structure. The darker of the two shows itself as a darkish yellow substance, very uniformly distributed throughout the field, comprehending the intervals between the bedding-planes, and stretching across these, but without disturbing their lamination. The optical outlines are indistinct, and towards the edges the whole mass assumes a cloudy aspect. In places the colour is much lighter, cloudy and indistinct, but differs from the second type of substance, to be presently described, in optical qualities and apparent structure.

The second type of resinoid material occupies considerable areas of the field, as laminæ, more or less irregularly spheroidal in shape. They are composed of homogeneous translucent and waxy looking material differing in its refractive index from the former, and with clearly defined optical outlines. But what is perhaps most dis-

tinctive is its possession of an internal structure, represented by what looks like cracks, occupying its surface, and apparently extending throughout the body of the laminæ. These resemble cracks and fissures in white wax when the material is subjected to strain, and may result from similar conditions affecting the laminæ.

The relative quantity of the two substances in the shale, as far as the specimens can determine, seems to be in favour of the former. The laminæ are seen to occupy considerable areas of the field, but do not disturb the bedding-planes. Both substances in a general way, but especially the latter, remind one of gelatinised scum, more perhaps than anything else.

Inorganic grains are present in all the specimens, mostly in the form of silicates of alumina with iron, potash and water, such as glauconite, several grains of this light green mineral being met with in the field, but not nearly so frequently as in the Kimmeridge of Dorset. Quite a considerable number of grains of mica are met with, besides many carbonates, probably of lime and iron. There are no sand courses visible in the specimen, such as are so frequently met with in ordinary shale.

No vegetable fossils are present, and very few organisms. In this respect the Norfolk specimens differ very decisively from the Boghead coals and torbanites. They more nearly resemble specimens from the shales of the Scotch Calciferous Sandstone series, but yet in internal structure, constitution, and type of material, they are by no means identical.

The similarity, however, is greater between Norfolk and Kimmeridge specimens in structure, the uniformity of the resinoid substance, and the shape and amount of the carbonaceous contents. In the Dorsetshire shales the outline of the bedding-planes is more distinct, and has a wavy contour with an almost entire absence of the waxy material present in the Norfolk beds. On the other hand the latter exhibit direct lamination with finer outlines.

The specific gravity of the Norfolk shale varies with the various fragments, doubtless owing to air inclusions. Four different fragments gave 1·397, 1·324, 1·403 and 1·260. When the material was crushed to thirty mesh, its specific gravity was 1·55. Its specific gravity, therefore, more nearly resembles the heavier class of torbanite or kerosene shale, which is 1·30. It is heavier than cannel coal, which is 1·26, or asphaltum, which is 1·2. It approaches nearer to Californian fuller's earth, which is 1·85 to 2·0.

Chemical Composition.

It is found when the shale is shaken up with ether that it is possible to recover as much as 1 % of oil, whereas when shaken up with carbon disulphide, the shale yields only 0·25 %.

A number of analyses have been made of the Norfolk oil-shale, during the progress of research work undertaken on the northern section of the outcrop. It has been found that the average volatile content in the two series is remarkably constant. Three analyses may be given as examples of the relative value of the two series.

	Smith's Series.	Puny Drain Series.	
Moisture	9·8	8·0	4·1
Volatile organic matter ...	35·1	31·7	37·1*
Fixed Carbon	15·3	16·3	12·0
Ash	39·8	44·0	46·8

Analysis of the inorganic contents gave the following results:—

	Moisture of water volatilised at 100° C.	4·100
	Calcium carbonate	8·800
	Calcium tri-phosphate $Ca_3 P_2 O_8$ (equivalent to $P_2 O_5$ 0·4%)	0·892
	Iron Pyrites (containing Fe, 1·22; Sulphur, 1·46)	2·680
	Alumina, soluble in hydrochloric acid	4·860
	Ferric oxide	1·510
Insoluble in Hydrochloric Acid.	Silica	22·680
	Alumina	4·620
	Ferrous oxide	1·380
	Lime and Magnesia	traces
	Sulphur unoxidised, probably in organic combinations...	2·860
	Total organic matter and combined water (by diff.)	45·618
		100·000

After roasting to oxidise fixed carbon, the analysis of the inorganic matter gave:—

Silica	49·50
Alumina	20·20
Ferric-oxide	10·27
Lime	11·68
Magnesia and Carbonic acid	1·22
Sulphuric acid	6·30
Phosphoric acid	0·83
	100·00

* Including combined water and organic sulphur.

After distillation of the volatile hydrocarbons, analysis of the coke gave residual sulphur 2·81 %. This tends to show that some of the organic sulphur is fixed by the earthy bases during distillation, as it is in excess of that which is due to the ferrous sulphide (FeS) which would result from heating of the pyrites content under the conditions of the distillation. Thus the sulphur that was eliminated with the volatile matter was about ·6, whilst that remaining fixed in the coke residue was ·4, of the 4·32. When a comparison is made between the inorganic contents of Norfolk shale after roasting, and the inorganic constituents of fire clays, brick clays, fuller's earth and spent Scotch shales, it is found that the Norfolk shales intimately resemble the latter. Especially is this the case in the silica, alumina and ferric oxide contents.

Analysis of organic contents.—The organic contents of the shale common to the Puny Drain are remarkably constant in amount throughout the series, both along the outcrop and on the dip. The oil in the Puny Drain shales appears to be derived from two different sources. First from indigenous material, possibly of animal origin, for the vast numbers of marine fossils of which the shales are so largely composed, especially the large degenerate Perisphinctoid type of Ammonites would be sufficient to allow of such an origin for a part of the oil being within the range of possibility. And secondly, the oil must have been derived from a source of free oil. Whether this is formed *in situ* as the result of the natural distillation of more deeply-seated shale beds and the rise of the resulting volatile products into the superficial and superincumbent beds, which are now exposed, or whether, as seems more probable, it comes from a source of liquid oil confined at a high pressure beneath the series, it is not yet possible to demonstrate. That free oil does exist is clearly shown by three classes of evidence. First, that as much as 1 % of oil is dissolved when the shale is treated with ether; secondly, from the prospecting side, when the limestone capping is penetrated, and water covered with oil appears in the sinking, or when a piece of shale recently broken out from the bed is subjected to running water, and the oil is seen to escape and form a scum on the surface; and thirdly, when the shale is treated in retorts, when it is found that the greater part of its oil contents comes off at a temperature under 300° C.

Physical character of the Oil.—The oil obtained from both series of shales is golden-black in colour, with a purplish tint by reflected lights. The oil is very fluid, running almost like water, despite the fact that its specific gravity is as high as ·942 to ·960. In this respect, it differs from the Scotch shale oil, which is dark-green in

colour, with a specific gravity of ·860 to ·890, and is very viscous, with a setting point of about 32° C. Norfolk Shale Oil differs likewise from oil derived from the Dorset-Kimmeridge series, both in its colour and in its viscosity. The specific gravity of the motor-spirit or petrol obtained from redistillation of the oil is ·855, with a low flash-point. Scotch Shale naphtha has a specific gravity of ·734.

Bulk tests carried out on Puny Drain shales, both in the field work erected near the outcrop, and in works under the supervision of engineers appointed by financial interests, gave highly satisfactory results. The yield of oil on a commercial basis was 40 gallons to the ton, the nitrogen content was about 1 %, and the yield of sulphate of ammonia was 66 lbs. per ton; while there was obtained 25,000 cubic feet per ton of dry gas possessing highly illuminating properties. The sulphur-content was as high as 6·4 %. The oil obtained on these bulk tests had a high specific gravity, namely, ·942 to ·960, was very fluid, and yielded on distillation:

Fractionation up to 100° C.	3·8	3·8
" " 100° to 170° C. ...	5·7	9·5
" " 170° to 245° C. ...	19·2	28·7
" " 245° to 310° C. ...	39·2	67·9
Water	0·8	68·7
Pitch & Loss	31·5	100·2

In the field trials, fractionation of the oil gave results as follows:

0° to 185° C.	23·3
185° to 250° C.	24·6
250° to 300° C.	20·8
Above 300° C. (by difference)	31·3

The yield of fractions coming within the limits of the motor-spirit series is considerable, and of the utmost importance. In addition, the oil yields from 3 to 4 % of bases extracted by weak acids, 3 to 4 % of crude phenols, cresols, etc., 3 to 4 % benzol and toluol.

The main interests of these bulk trials is the extremely low temperature at which the shales yield a big proportion of their oil contents, and that the residues contain 20 to 27 % of carbon, fixed and unfixed.

Sulphur-contents.—It is impossible with the above data available for analysis to be any longer sceptical as to the value of the shale that will produce an oil in such quantities, and of such quality, containing so many by-products. Only one factor may be conceived to affect the value of the deposits, and that is the quantity of the sulphur-contents, which vary from 4·32 to 7·8 %. Here the shale

conforms to the known sulphur-contents of the Kimmeridge series generally. An interesting light is thrown on the question as to the form in which the sulphur is contained in the shale, by the analysis of the inorganic and organic constituents. There it is shown to be in two forms, organic and inorganic, and that part of the organic derivative seems only to be held by the inorganic bases during distillation. Although the elimination of the sulphur from the Kimmeridge shales has been found a difficulty, it need not be inferred that it is insurmountable. There are already indications from more than one quarter that methods are in being to effect this object. The sulphur-contents of the Norfolk shales do not seem to be obstinately "held." And already it has been possible in the laboratory to effect the elimination of the sulphur-contents to below the figure (namely 3 %) sanctioned by the Admiralty. It is a step in the right direction, and there does not appear to be any reason why similar success should not be obtained in commercial practice, or, indeed, that practically the entire sulphur-contents should not be eliminated in the immediate future. Still, in view of the fact that there are oil-shales which are found difficult to treat for the sulphur incorporated therein, it seems from a practical point of view that a great deal has been made of the sulphur difficulty. Evidence is to hand that shale oil containing as much as 4 % of sulphur has been used in internal-combustion engines without any trouble resulting, and in steam-boilers it is, of course, very much less. For steam-raising, coal with over 2 % sulphur is regularly employed. Even Welsh coal has an average of 1·43 %. Weight for weight much less oil than coal is required, and therefore, relatively, less sulphur is liberated in the fire-box. One ton of fuel oil containing 4 % of sulphur will liberate in a boiler furnace 90 lbs. of sulphur. The equivalent of coal containing 2 % of sulphur is roughly 82 lbs., a trifling difference of no practical importance.

Extent of Oil-shale Fields in Norfolk.

There is little doubt that a large oil-shale basin of Kimmeridge time exists in Norfolk. The evidence for such belief rests upon an analysis of the structure of the east of England when brought into alignment with known tectonic conditions within the area. Its geographical extent has not yet been completely demonstrated, although its visible geological features have been traced for many miles north and south, and for considerable distances on the dip. The possibility of the Kimmeridge series being cut off against the edge of the chalk has not been lost sight of, but all research work in this direction goes to prove that the Kimmeridge beds dip under-

neath the chalk. No signs of faulting, such as cuts the Kimmeridge beds, and brings them against the chalk at Ridgeway, in Dorset, can be observed in the eastern section of the Wormegay basin. The boring at Holkham, 743 feet deep, is said to have terminated in Kimmeridge clay, although another version makes it terminate in Lower Greensand. Nevertheless, adjacent and available data lead to a belief in the permanence of the Kimmeridge beds, beneath and seaward of the chalk shore line at Holkham and Hunstanton.

With a proved thickness of 6 feet of oil-shale in Smith's series, and 6 feet in the Puny Drain series, or a total of 12 feet, every acre of ground should yield something like 24,000 tons of shale, and half a square mile may be considered as providing for a 1,000 ton output per day for 20 years.

But with every indication that this estimate will be quadrupled or more, and with a possible extension of the basin, very far beyond its present indefinite limits, it is obvious that the oil contents of the Norfolk end of the Kimmeridge outcrop will add very considerably to the oil resources of the United Kingdom.

Such a conclusion, which is borne out by careful examination of all authentic data, and by patient and laborious research in the field, implies that England is not so entirely destitute of oil resources as many people suppose. In the near future, the oil-fields of the Kimmeridge outcrop may be supplying a considerable bulk of the oil and petrol consumed in this country, and will enable the large amount of gold sent abroad every year to pay for foreign oil to be considerably reduced. This in itself is a matter of great importance from the view of national finance. The whole question of the English Kimmeridge measures demands investigation, for where one great productive basin exists in the south extremity of the Kimmeridge outcrop, and another great basin at the other, there is no adequate reason, yet presented, why there should not be other large productive basins in existence, between these two geological terminals.

It is a national question. Private individuals have done much to demonstrate great deposits of oil in specific parts of these measures. The State, through the exigencies of war, is approaching that communal ideal when it may be called the Mother of its citizens. Let it deal therefore with this most important economic question, the question of an internal supply of oil fuel, which more and more tends to underlie industrial efficiency, military and naval power, and might in the immediate future of the race comprehend even the basis of national existence.

DISCUSSION.

The President, in opening the discussion, said the members had just listened to a paper of considerable interest on a subject which, as the author rightly stated, was one of Imperial importance. The subject had been under the consideration of the Council, and it would be in the recollection of the members that two Committees had been appointed to deal with two of its branches, which had been very prominently referred to by the author, namely, the possibility of the existence of oils in oil-shales within the British domain, of which Committee the author was a member, and secondly the elimination of sulphur from oils, particularly oils obtained from shales. The latter Committee was already actively engaged in undertaking investigations upon the problem. The material which had been put before the members specifically dealing with the Norfolk oil-shales was of considerable national importance. Whether the developments which were outlined by the author would produce the particular volume of oil which he predicted was a matter which could only be proved after very serious consideration and test. He desired to direct the attention of those who were studying the subject of the origin of oil-shales to what appeared to him to be a very important paper which had recently been written by Mr. Graham, of the Doncaster Coal Owners' Laboratory, in which he had clearly demonstrated that a gas might dissolve in a solid. That matter was well worthy of the attention of those who were studying the subject, in that it certainly threw some light upon the great problem of the origin of petroleum.

Sir Boverton Redwood (Past President) said that his only qualification for accepting the invitation to say a few words was that he had been privileged to study the detailed records of the research work which had been carried out during recent years by the author in the region specially referred to in the paper, and he had been deeply impressed with the painstaking character of the investigations which the author had conducted. He felt justified in saying that the data which had been so ably presented to the members in this most instructive paper were in no sense of an imaginative character, but were based upon quite exceptionally patient and systematic investigation. He ventured to think therefore that there need be no hesitation in accepting the views of the author as to the existence in Norfolk of abundant supplies of exceedingly rich oil-shale, yielding nearly double the quantity of oil to the ton that was obtained at the present time from the average of the oil-shale worked in the Scottish refineries. But it

must be borne in mind, as the author pointed out, that the oil was of a very different character from that yielded by Scottish oil-shale. It was *sui generis* in many particulars, which had been indicated in the paper. There were no doubt industrial problems connected with the utilisation of the oil which would demand as patient an investigation as that which the author had already devoted to the subject of the occurrence of the shales. Prominent among the various problems which the unique character of the oil presented for solution was that of the elimination of the sulphur, which, as the author very candidly admitted, had in the past presented difficulties. He had at a previous meeting of the Institution expressed the view that it was most unlikely that chemical science would fail to solve that problem, and he saw no reason why failure should be anticipated. On the contrary, he knew of more than one process which had already given highly encouraging results, amounting, in point of fact, to the reduction of the sulphur-content to a figure considerably below that mentioned by the author. He had great confidence that the Committee which had been appointed by the Institution to deal with the subject would before long be in a position definitely to announce that the problem in question had been successfully solved. He desired to say in conclusion that he had listened to the paper with great interest, and thought that the Institution was to be congratulated on having been the first recipient of a great deal of information not hitherto published in connection with a matter of industrial importance to the nation.

Dr. A. E. Dunstan said there were a few questions of detail from the chemical standpoint that he desired to ask the author. He had said, for instance, that when the shale was shaken up with ether it was found possible to recover as much as 1 per cent. of oil, and when shaken up with carbon disulphide, the shale yielded 0·25 per cent. It was a well-known fact that coal was in like manner partially soluble, and he believed that Professor Wheeler had already isolated paraffin wax from coal. It would also be of interest if the author would state the nature of the extracted oils, and whether any chemical work had been done on the subject of their constitution. Professor Wheeler rather suggested that compounds existed in coal which might be described as partially aromatic and partially paraffinoid oil. Possibly there was a benzene nucleus attached to the paraffin nucleus. Professor Wheeler contended that those substances on distillation broke down readily, and were the source of the aromatic compounds produced in coal-tar. A further point that struck him was the partial elimination

of the sulphur by the bases in the inorganic residue. That being the case, it was conceivable that the addition, in the retorting, of lime or some other base might have some effect in reducing the sulphur-content. It was practically certain, he thought, that the question of the de-sulphurisation of shale-oils would ultimately be solved, because at the present moment there were indications from a variety of sources and a variety of standpoints that the subject was being attacked in a way that rendered it certain that the problem was well on the way to solution. The difficulty experienced was that the sulphur-compounds in the shale-oils were associated with hydrocarbons of about the same degree of affinity, and, so far, the ordinary routine method of separation, which depended on the superior reactivity of sulphur-compounds, had failed. A very curious point occurred in connection with the high specific gravity of the products. He noticed that the petrol was stated to have a specific gravity of 0·855. The aromatic hydrocarbons occurring at that range of boiling points, benzene and toluol, had a specific gravity of 0·882 and 0·870, which rather suggested that in the shale-oil from Norfolk there were possibly more aromatic hydrocarbons than the 2 or 3 per cent. referred to by the author, or that the unsaturated hydrocarbons, with their well-known high specific gravity, were present to a very considerable extent; consequently somewhat skilled chemical handling would be necessary in refining. Finally, a highly interesting point occurred in connection with the occurrence in shale-oil of phenols and cresols and bases soluble in dilute acid. He found that in 1870 the Scottish shale-oil was entirely destitute of aromatic compounds, of phenols and cresols, but from time to time the retorting temperature had been raised, and Steuart in a recent paper pointed out, as the author had done, that phenols, cresols, and other aromatic compounds were of quite common occurrence. He believed the temperature of the retorting of the Norfolk shale had been quite low. (**Dr. Forbes-Leslie** said that that was so.) **Dr. Dunstan** said in that case it was difficult to account for the appearance of substances which usually occurred at very high retorting temperatures.

Mr. Cunningham Craig said there were a great many points in the paper that he would like to discuss, but he would confine himself to only a very few of them. In the first place, he desired to congratulate the Institution upon having received such a paper. In spite of all that had been said, he felt that the members might be in danger of forgetting its importance. Our poor old country has been paying through the nose for foreign oil for he did not know how many years, and it had had to set up a Petrol Control

Committee to prevent users from getting the petrol which was in the country and which they wanted badly, but which they were not allowed to have. On the other hand, the author had shown that there was probably an enormous source of oil in this country, although it was not absolutely proved over a large area. Something had been known about it in Dorsetshire since Elizabethan times at any rate, and yet practically nothing had been done. The people of the country had lived above it, and had let it stay there. It was only during the period of war, when people had begun to think of what existed in the country, and what they could do in the way of using the products lying under their feet, that much attention has been given to the subject. The petrol referred to in the paper had a specific gravity of 0·855, which would bring it outside the Petrol Acts, so that it might be used without the Petrol Committee putting any embargo upon it. The geological points raised by the author were particularly interesting, but, much as he would like to dilate upon them, he would not do so. Reference had been made to the free oil that had been actually seen on the surface of the water, and the bituminous impregnations in their sandstones which occurred below some of the shale seams. When such things occurred in Scotland, his friends there said, "Oh, there has been an igneous rock there, which has distilled the oil, and hydrocarbons have condensed in the porous rocks." In the present instance there was no possible likelihood of there being any igneous rock concealed, but in Scotland when they did not see any igneous rock they assumed its presence underneath. He could not help thinking that the author had done a good deal to help forward a little theory that he (Mr. Cunningham Craig) put before the Institution in April. Since that meeting he had conducted certain researches with the microscope upon oil-shales and allied deposits, both from this and other countries, and although he had not seen any microscopic sections of the Norfolk shale he hoped that the author would show him some soon. From an examination of the Dorset shale he had found some very interesting points of resemblance between it and the New Brunswick shale, the Scottish kerogen shale and inspissated shale oil; in fact, he had found so little essential difference between the various deposits that he could show a gradation from one to the other. He did not know whether the author exactly claimed that the Norfolk shale was a kerogen shale, and whether he might not even offend their Scottish friends by using the word "kerogen" in connection with the shale; but, quite apart from the importance of describing a district in Norfolk where rich oil-shales could be found, the author had added a

great deal to the general understanding of the very important question of the origin of oil-shales and deposits of like nature throughout the world.

The President, introducing Dr. Hume, the Geological Adviser of the Egyptian Government, and in welcoming him, hoped he would join in the discussion, but **Dr. Hume,** after thanking the President and members for the very kind welcome they had accorded to him, said that he had no special knowledge on the question before the meeting, and had simply listened to the paper as a learner.

Mr. W. H. Manfield desired to ask the author, firstly, what evidence he had found, and where, of any metamorphism of the Kimmeridge measures in Dorset, apart from any that might have been caused by the fire at Ringstead. It was very peculiar that the two series the author had mentioned were so much alike, the upper series containing a shale of 6 ft. in thickness, and yielding 50 gallons of oil per ton; and the lower, one of practically the same thickness, and giving the same yield, although the evidence advanced seemed very strong in favour of their being quite separate the one from the other. He would be glad to know if either sample was taken from a very much greater depth than that taken from the other series, because it was noticeable in Dorset shales that samples taken from the same bed at the outcrop, and at some depth differed very considerably in colour, in appearance, and also somewhat in texture. He did not wish to deprive the author of a valuable bed of shale, but from what he saw of the measures when he was in Norfolk, the position of the beds was somewhat involved, and difficult to trace, and he hoped that, before the author gave his second paper on the subject, a borehole would be put down which would not only prove the top seam, but also go through to the lower seam, so similar in thickness and yield. He was very glad that the author had discovered and to hear such strong evidence of the presence of free oil in the Kimmeridge measures in Norfolk. That had not yet been demonstrated in Dorset, although he hoped that some day free oil would be discovered there also.

Dr. Leo Henderson said the paper appealed to him as a record of facts, the result of valuable research work on a subject of national importance. The facts brought forward by the author raised many questions of interest to petroleum technologists. The occurrence of free oil occurring within the shale beds, and particularly immediately below the overlying limestone, reminded him of a similar phenomenon on a much larger scale, which he had

observed when drilling through a very thick series of shales exceeding 2,700 ft. in thickness of Lower Carboniferous age, the Albert Shales in New Brunswick. In this case in certain boreholes flows of natural gas, accompanied by liquid oil in appreciable quantity, were encountered issuing from certain bedding-planes of the shale beds, usually at the base of hard calcareous bands. These flows occurred in groups within certain horizons along which lay corresponding interbedded series of lenticular sandstones highly charged with gas and oil, which thinned out at distances varying from a few hundred to one or two thousand feet from the boreholes whence the flows took place. The shales in themselves carried no free oil, although within distinct zones well-defined highly-bituminous layers were found. This migration of liquid oil and gas along bedding-planes from reservoir rocks was interesting, and he would like to know whether any indications of interbedded sandstone had been found within the Norfolk shales, other than that mentioned by the author. In his opinion it would be of advantage if the author could give more details regarding the included sandstones referred to by him; for instance, their position on the anticline, their thickness, nature of the grains, cementation, whether containing fresh or salt water, and so forth.

The occurrence of free oil and bituminous substances within the Puny Drain shale bed, composed as it appears to be almost wholly of fossils of marine type, impressed him as being of unusual interest in considering the origin of petroleum. Of the oil-shales which he has examined in Australia, South Africa, America and Scotland, the bituminous matter appeared in the majority of cases to be largely of vegetable origin. The Norfolk Puny Drain Shale, however, appears from the author's description and chemical tests, to be of animal origin, and the oil distilled from it to possess a character different from that of oil obtained from ordinary oil-shales. In this connection he did not know if the author was aware of recent interesting evidence regarding the formation of oil *in situ* from marine organisms, which was furnished by shell beds of recent age on the subarctic Alaskan littoral. That trained observer, Mr. T. A. Rickard (*Min. Mag.*, vol. xi, p. 252, 1914), in describing the beach-placers of Nome, Alaska, has recorded the fact that shell beds, where penetrated by the alluvial gold diggers, yield sufficient oil to interfere greatly with the recovery of gold from the associated auriferous sands and gravels through the adherence of the oil to the fine gold, and the consequent effect on the relative gravities in the washing process. Careful investigation of such deposits by those interested in the scientific as well as in the

practical aspect of petroleum technology, may throw light upon the question of origin and accumulation of petroleums.

Mr. W. A. Butterfield desired to remark that the high specific gravity of the motor-spirit seemed to indicate a large proportion of aromatic hydrocarbons. If that was the case, the question of the elimination of the sulphur should not be such a difficult one as in the case of oils consisting chiefly of aliphatic hydrocarbons, particularly paraffins. It was not so many years since benzol refiners found great difficulty in eliminating thiophene from benzene, and he thought possibly the use of their present methods might result in the elimination of a considerable proportion of the sulphur from shale-oil. He had wondered whether there was not some fallacy underlying the observation of the author in his comparison of the amount of sulphur liberated in the fire-box when a boiler was fired by oil fuel containing 4 per cent. and by coal containing 2 per cent. of sulphur respectively. He had not worked out the figures, but he wondered whether the author had borne in mind that, of the sulphur in the coal, probably not more than half went off in the products of combustion, the rest being retained in the ashes and clinker; whereas in the case of the oil fuel the whole of it went into the products of combustion.

Dr. William Forbes-Leslie, in reply, said he would deal first with the question raised by Mr. Manfield on the subject of metamorphism. There was no question of metamorphism in the way in which that term was used in this country, but he believed there was in America a reference to an incipient form of metamorphism which did not affect the crystallisation of the rock in any way; it simply meant that the rock was drier and more consolidated, and lost colour. He had samples with him of the two seams of shale, which the members would have an opportunity of inspecting, and it would be seen that the Dorset shale was undoubtedly more compressed than the Norfolk shale. It seemed to have been affected by higher pressure, probably at greater depths. The two seams of shale were quite distinct in character; they were not the same bed, and the samples were taken at about the same distance from the surface: it was not a question of weathering.

With regard to Dr. Henderson's question on the subject of sandstones, evidence existed at the present moment of a considerable body of sandstones in Norfolk, and he hoped to bring that point forward in a subsequent paper. At the present moment he thought it was a little too previous to talk about it, but he thought he would have something to say on that subject which would prove of interest to the members.

He had not seen the very interesting account of gold diggers discovering oil associated with gold, to which Dr. Henderson had referred. Sometimes oil would prove more profitable than gold. But the point was very interesting, because the Norfolk shales were full of fossils,—so full that in some cases they could almost be called shell beds, and there was therefore a certain amount of resemblance.

With regard to Dr. Dunstan's questions, as Mr. Wells was present at the meeting, and had been more or less responsible for the chemical distillation tests, he would be able to reply to Dr. Dunstan's remarks better than the speaker.

Mr. Butterfield had raised a very interesting point, to answer which it would be necessary for him to refer to his figures. There might be a fallacy, as Mr. Butterfield suggested. He would reply more fully to the question at a subsequent meeting. In conclusion, he desired to thank the members very much indeed for the kindly way they had listened to his paper, and the patience they had shown towards him.

Mr. J. Wells, in reply to Dr. Dunstan's question, said that very little could at present be said in regard to the various fractions obtainable. Only preliminary distillation work had been carried on at low temperatures, several tons having been put through, and he did not think the results obtained were those that would ensue in actual practice. It was very largely a question of the temperature at which distillation took place as to the yield of aromatic compounds. The higher the temperature used, the more gases were formed, and the more saturated were the products obtained; the lower the distillation temperature, the higher was the percentage of unsaturated hydrocarbons. The tests were made in horizontal retorts in which the temperature immediately at the end of the retort never exceeded 450° F. Under those circumstances, it was found that the specific gravity was very high, though the oil was extremely mobile but readily attacked by acid. Even quite a weak acid wash would destroy a large percentage of it. He thought it was very largely a question of the temperature at which the distillation was carried out, and until experiments were made on several thousand tons he did not think they would get much forwarder. The whole question of distillation system has yet to be developed, and the ultimate value of the shales is wrapped up in this matter.

The President said he was sure the members would not wish him to close the meeting without expressing their very cordial appreciation of the excellent paper the author had read. It had

involved an enormous amount of work and very careful research, and the members were extremely indebted to the author for bringing it before them. On behalf of the Institution, he thanked Dr. Forbes-Leslie most heartily for his very able paper.

The meeting then terminated with hearty expressions of approval, and inspection of the samples of shale, oil, etc.

The Mexican Oilfields.

[Abstract of remarks by Mr. W. CALDER on Mr. Stewart's paper in vol. ii, pp. 7–43.]

IN reference to the range of seepages from Tamaulipas to Tabasco, he holds the petroleum industry of the country to be still in its infancy, its growth checked by political conditions.

The oil probably occurs mostly in small isolated pools under great pressure, causing natural flow, on the cessation of which the remaining store will not pay for artificial extraction. But some of the first-tested areas are still yielding, and their life is likely to be prolonged.

In some parts, high-grade oil occurs over large areas, where, though no huge producers may be struck, the quality and wide distribution will be compensatory factors.

For prospecting, he recommends *dry* drilling, in order to detect the earliest indications of gas or oil, and take the necessary precautions. The statutory compulsion of working through a gate-valve after 1,800 feet is difficult to enforce with ordinary drillers.

In the crater formed by Dos Bocas No. 2, one of the "wonders of the world," outbursts of gas occurred at times stated as mostly from 1 to 3 p.m., and 12 to 2 a.m., the fountain in the centre rising gradually to 30 feet above the water-level. The night eruptions were the more violent, with a noise like distant thunder, and large quantities of sulphurous gas, perceptible at the camp a mile distant. May there not here be some connection with the cause, suggested as earth-movements, of falls of roof in mines, most frequent about the same hours of 12 to 3 a.m.?

[In a seismic region like Mexico, crustal movements, of quasi-tidal periodicity, may reasonably be expected to recur, and these would necessarily affect the fluids, gas, oil and water, present under pressure in subterranean spaces.—ED.]

Seventeenth General Meeting.

The Seventeenth General Meeting was held at the House of the Royal Society of Arts, John Street, Adelphi, W.C., on Tuesday evening, 21st November, 1916, Prof. John Cadman, C.M.G., D.Sc., M.Inst.C.E., President, occupying the Chair.

The Members of Council present were: Messrs. Andrew Campbell, E. H. Cunningham Craig, Arthur W. Eastlake, Dr. F. Mollwo Perkin and Sir Boverton Redwood, Bart. A letter of regret for unavoidable absence was received from Mr. T. C. Palmer.

A paper on "the pyrogenesis of hydrocarbons" under the joint authorship of Mr. E. Lawson Lomax, Dr. A. E. Dunstan, and Dr. F. B. Thole, D.Sc., F.C.S., had been set down for reading and discussion, and before calling upon Mr. Lomax to commence reading, **The President** remarked that it was unnecessary for him to remind the audience of the high status of the authors. He would however draw attention to the evidence of efficiency conveyed in the fact of collaboration of such recognised authorities in a work of such importance. Scientists were often too prone to maintain an attitude of jealous isolation, although such might in some cases be advisable. Healthy collaboration of the nature to be exhibited that evening was calculated to effect rapid progress.

Mr. Lomax then summarised his section of the work, which was illustrated by numerous slides, showing the various systems of operation, and was followed by Dr. Dunstan, who dealt similarly with the second portion, contributed by Dr. Thole and himself, using ingenious models to illustrate the relations and reactions of the elements composing the hydrocarbons under discussion.

The Pyrogenesis of Hydrocarbons.*

By E. Lawson Lomax, M.Sc., F.C.S., A. E. Dunstan, D.Sc., F.C.S., and F. B. Thole, D.Sc., F.C.S., *Members.*

Part I.—*Historical and Bibliographical.*

By E. Lawson Lomax.

In submitting to the Members of the Institution the following papers on "Pyrogenesis of Petroleum," we have endeavoured in a general way to illustrate the various stages through which development has taken place.

* Numbers appended to names of authors mentioned are those of entries in the bibliographic indexes, pp. 90–96, the attached *a* denoting the literary section, its absence that enumerating patents.

The subject, however, is so vast that it is impossible adequately to deal with it in a single evening, but we hope at some future date to have the honour to present to you in greater detail some of the features of the particular processes or types of processes which are being worked at the present time.

The products of the pyrogenetic treatment of petroleum may be divided into four general classes, viz.: permanent gas: illuminating oils: aromatic hydrocarbons: and volatile fuels for internal-combustion engines. These classes also represent roughly the lines on which development has taken place.

Although the manufacture of permanent gas is of secondary importance to we as an Institution, the earliest work on the pyrogenesis of petroleum was started with this end in view, and it is as well briefly to refer to the pioneer work on the subject. The use of illuminating gas made from oil was proposed as early as 1792 by Murdock, and in 1805, as well as in 1821, Henry [2a] described the gas obtained by cracking animal oils, fats and waxes, noticing the formation of ethylene. Between these two dates, John Dalton [1a] in 1809 carried out the first scientific investigation on the pyrogenetic decomposition of hydrocarbons by subjecting ethylene and methane to the action of electric sparks.

It is evident that about this time the question of the production of gas from oil occupied the attention of inventors and scientists; for a few years later, in 1825, we have the classic discovery of benzene by Faraday [3a] in the products obtained by action of heat upon oil, during the course of which work he also noticed the presence of unsaturated hydrocarbons which are very reactive to sulphuric acid.

The work of Dalton on the decomposition of ethylene and methane by electric sparks inspired later workers on the same lines such as Marchand [4a], Magnus [5a], Quet [7a], Hoffmann and Buff [8a], and De Wilde [13a], who all worked on the decomposition of ethylene by heat, and described some of the products of the reactions.

In 1866—1867 the famous French chemist Berthelot [13a, 14a, 15a, published the results of a brilliant series of researches on the action of heat on various hydrocarbons. He showed that acetylene heated alone in a closed space at the temperature at which glass softens, is decomposed, forming liquid hydrocarbons, 97 % of the acetylene having disappeared at the end of 30 minutes. In the presence of coke, acetylene is decomposed almost wholly to carbon and hydrogen, and in the presence of iron, half of the hydrogen is released in a free state with the formation of empyreumatic hydrocarbons, the reaction proceeding more rapidly,

and at lower temperature. When acetylene is mixed with other gases, such as hydrogen, methane, ethane or carbonic oxide, the reaction proceeds more slowly, and ethylene is formed.

He also showed that the action is reversible at higher temperatures. Under the same conditions :—Ethylene gave ethane, acetylene and tarry products. Ethane gave ethylene. Ethylene and hydrogen in equal parts gave ethane, and at dull red heat equilibrium was established between ethylene, hydrogen and ethane. Acetylene and ethylene in equal parts gave as principal product a body which was either an isomer or identical with crotonylene. Acetylene and benzene in equal parts gave naphthalene.

At this temperature, which he presumed to be 600°—700° C., hydrocarbons react by direct affinity, and, starting with the lowest hydrocarbon, all the members of the series can be synthesized.

In a later paper he gives the results of passing various hydrocarbons through a porcelain tube heated to bright redness :—benzene gave di-phenyl, chrysene and a resinous body, but no anthracene or naphthalene. Toluene gave benzene, unaltered toluene, naphthalene in large quantity, a crystalline hydrocarbon volatile at 270° C., a large portion of a liquid hydrocarbon which he called benzyle, also anthracene and bodies analogous to chrysene. Benzene and ethylene mixed gave styrolene, naphthalene and anthracene. Styrolene gave benzene and acetylene. Styrolene and hydrogen mixed gave benzene and ethylene. Styrolene and ethylene mixed gave principally naphthalene and some benzene. Styrolene and benzene mixed gave principally anthracene, also naphthalene and di-phenyl. Benzene and naphthalene mixed gave anthracene. Di-phenyl gave benzene and chrysene. Xylene gave toluene as principal product, also benzene, naphthalene, anthracene and unchanged xylene. Cumolene gave toluene and xylene in large quantities ; also benzene, cumolene, naphthalene, anthracene, chrysene and benzerythrene in smaller amounts. The results of this work stand to the present day, the whole study being worthy of the great author.

Shortly before this, the attention of the oil industry was directed to the question of increased production of illuminating oils by "cracking," an operation which was accidentally discovered in 1861 owing to the carelessness of a stillman, who built a strong fire under his still, and left it running, intending to return in about an hour. He did not, however, return till about four hours later, when he found the still running a light coloured distillate of lower specific gravity than that which was passing when he left.

Experiment showed that a portion of the distillate had condensed upon the upper cooler part of the still, and, dropping back on to the hot residue was decomposed into lower-boiling constituents.

This discovery had, however, to some extent been anticipated by Silliman in 1855 [6a], who advanced the theory that several of the products of distillation of petroleum were results of heat and chemical change during distillation. The discovery led to a large amount of technical and scientific work on the increased production from petroleum of illuminating oil, which at that time was the most valuable product obtained.

In 1865 Young [3] took out a patent for increasing the yield of burning-oils by distillation under a pressure of about 20 lbs., which was followed in 1866 by that of Vincent and others [4], in which the vapours were partly cooled at the still-head, the condensates being allowed to fall back on the hot residues; and a provisional patent in 1869 by Scot and MacIvor [7].

In the meantime, the question was being discussed by Hirsch [17a], Silliman [18a], and Peckham [19a], from a theoretical standpoint; an account of his process was published by Young in 1867 [16a], which was followed in 1871—1873 by the famous researches of Thorpe and Young [21a] on the effect of distilling solid paraffin under pressure, together with a description of products formed boiling below 200° C., these products consisting of paraffins and olefines as follows:—amylene, pentane, hexylene, hexane, heptylene, heptane, octylene, octane, nonylene, nonane, undecylene, undecane and possibly caprylidene, but with no trace of benzene.

An interesting item in connection with this research was communicated to us by your Past President, Sir Boverton Redwood, to the effect that it is not generally known that this research of Thorpe and Young was carried out with a view to determining what actually took place during distillation as carried out according to Young's Patent of 1865 [3].

In 1864 and 1865 Vohl [10a & 11a] describes the treatment of heavy petroleum residues by passing them through hot tubes packed with lime or iron filings, in order to obtain burning oils.

Previous to this, attempts had been made to utilize the tars formed in the manufacture of oil-gas for the production of aromatic hydrocarbons.

In 1860 a patent with this end in view was taken out by "Le Société pour l'éclairage au Gaz [1]," followed by that of Breitenlohner [2] in 1863 while in 1862 Veith [9a] describes the production of aromatic hydrocarbons by passing petroleum residues through iron tubes heated to 700°—800° C.

In 1877 Jacobsen [23a] showed that by the condensation of allylene and acetylene the seven benzene homologues present in coal-tar can be formed, and in the same year Cabot [24a] showed that no phenol or cresol is formed in making oil-gas, this being confirmed in 1881 by Rudnew [25a]. A year later Letny [26a], Liebermann and Burg [27a], and Salzmann and Wichelhaus [27a] published, almost simultaneously, accounts of processes for the production of aromatic hydrocarbons from Russian oil residues, by passing them through red-hot tubes with various packings. Letny claimed priority for these processes. Aromatic hydrocarbons, from benzol to anthracene, were obtained by Anschütz [28a], who claims that many of the more complex hydrocarbons are formed by condensation, with elimination of hydrogen: $2C_7H_8 = C_{14}H_{10} + 3H_2$.

In 1879 Prunier [29a] published results of researches on the pyrogenetic treatment of American oils, stating that the degree of saturation of the resulting products varies with the temperature, pressure and time of reaction. He isolated acetylene, butylene, crotonylene, benzene, styrolene and bodies similar to naphthalene and acenaphthene.

In 1884 Greville Williams described [34a] and took out a patent [19] for a process for separating aromatic hydrocarbons from the tar produced during the manufacture of oil-gas, and almost simultaneously Armstrong and Miller [35a] published the results of their well-known investigation on the liquid obtained by the compression of oil-gas, followed two years later by the examination of the gas itself and of the tar deposited prior to compression. In these investigations they isolated benzene, toluene, *o*–, *m*–, and *p*–xylenes, mesitylene, pseudo-cumene, naphthalene, crotonylene, isoallylethylene, ethylene, propylene, amylene, hexylene, and heptylene, with only traces of paraffins and naphthenes, and also showed that the unsaturated compounds are easily polymerized, these hydrocarbons, when freshly made, being volatile in steam. They stated that at the higher temperatures required for oil-gas manufacture, normal paraffins are completely decomposed into olefines, acetylenes, benzenes, etc., and that it is not improbable that the benzenes are products, in a direct line, of the action of heat on the paraffins, and not built up from hydrocarbons of the acetylene series.

In 1885 Redwood [36a] described the manufacture of aromatic hydrocarbons from Russian ostatki as carried out by Nobel Bros., by means of which benzene, naphthalene and anthracene were obtained, while in the same year Hirzel [14] secured a patent for the production of aromatic hydrocarbons by passing petroleum

vapours through a retort packed with porous material and heated to red heat, which is apparently the first attempt at pyrogenation in the vapour phase as distinct from the vaporization and pyrogenation in the same retort. A patent was also brought out by the Riebeckschе Montanwerke [16] in which it was claimed that by distilling oil under a pressure of 3—6 atmospheres, the yield of light oils was increased and the residues could be used for the preparation of lubricants.

Nikiforoff's well-known patent [17] in which the oil was decomposed in two stages, the first stage being at a temperature of 525°—550° C. in cast-iron retorts, and the second at 700°—1200° C. under a pressure of two atmospheres in retorts similar to those employed in the Pintsch gas process, was brought out in 1886, claim being made for a 12 % yield of benzol as well as other aromatic hydrocarbons [87a], and in the same year Burns [18] took out a patent for a process in which the oil-vapour from a special still was decomposed in retorts packed with scrap iron and coke.

The American chemists, Norton and Andrews [87a], studied the action of heat on hexane, isohexane and pentane. Hexane decomposed at a bright-red heat gave ethylene, propylene, butin (butadïene), amylene, hexylene and benzol as well as small quantities of saturated hydrocarbons boiling between 100°—160° C.

Treated at 550° C., hexane was not decomposed; at 600° C. there was no formation of gas, but the recovered hexane contained traces of unsaturated compounds, while at 700° C. decomposition with the evolution of gas took place and propylene, butylene, amylene, hexylene and butin (butadïene) were formed, but no benzene.

Iso-hexane decomposed at bright-red heat gave ethylene, propylene, butylene, amylene, hexylene and butin (butadïene).

Normal pentane decomposed at bright-red heat gave ethylene, propylene, butin (butadïene) and traces of other unsaturated hydrocarbons.

Day [89a] showed that ethylene begins to decompose when heated at 350° C., and that when heated at 400° C. for a sufficient time, it is entirely decomposed, with the formation of methane, ethane and liquid products, while Norton and Noyes [89a] showed that at low red heat ethylene gives benzol, naphthalene, propylene, butylene, di-vinyl, methane, ethane, carbon and possibly anthracene, the di-vinyl being similar to the crotonylene identified by Armstrong and Miller and the butin of Norton and Andrews.

Krämer and Böttcher [69a] in 1887 stated that aromatic hydrocarbons are formed by superheating aliphatic hydrocarbons or

by heating them under pressure but that under the same condition naphthenes are not formed.

Studying methods of increasing yields of illuminating oils from petroleum Lisenko [48a] found that when petroleum is distilled, it is not only split up into its constituents, but certain parts of the higher-boiling fraction are decomposed into bodies of lower boiling-point, the yield of these varying with the time of heating. By heating residues from Caucasian petroleum at 434°—501° C., the yield of kerosene was increased by 30 %.

Benton [19] took out a patent for this purpose in which the oil was heated in a coil at 371°—537° C. under a pressure of 500 lbs. per sq. in., and then led into an evaporating chamber connected with a condenser; while in 1889 Redwood and Dewar [20] patented their well-known process for increasing the yield of light oils from residues by distillation and condensation under pressure. This process gave very good results while it was worked. It was designed with a view to increasing the yields of kerosene from Russian oil, and thus decreasing the amount of ostatki produced, which was then somewhat of a drug on the market, but the employment of ostatki as a fuel came into prominence about this time, and it became as valuable as the kerosene which was produced from it, and so the process was abandoned for the time at least.

The demand for a motor-fuel to replace petrol had not yet arisen, so the work in the next decade was confined to the production of aromatic hydrocarbons, and to scientific investigations of the products formed by pyrogenetic treatment of petroleum hydrocarbons, the researches being carried out on both simple hydrocarbons and mixtures thereof.

In 1892 [49a] and again in 1894—1895 [50a] Lewes published the results of his investigations on the decomposition of ethylene, in which he states that if ethylene is passed through a tube heated to 800°—900° C. it is decomposed to acetylene and methane—

$$3C_2H_4 = 2C_2H_2 + 2CH_4.$$

If the products are maintained in the heat zone, the acetylene is polymerized to benzene; on raising the temperature to 1000° C. the benzene gives naphthalene, which on further heating to 1100° C. is decomposed to acetylene, which in turn breaks down to carbon and hydrogen. At 900° C. ethane gives up hydrogen with the formation of ethylene. He also showed that aromatic hydrocarbons are present in the tar formed, as well as possibly normal hexane, hexylene, normal heptane, heptylene, and nonane.

Boissien [48a] showed that mazout on dry distillation yielded

aromatic hydrocarbons, Dvorkovitz [47a] also showed that in the manufacture of oil-gas large amounts of aromatic hydrocarbons were obtained, and in 1894 Noyes, Blinks and Mory [48a] examined oil-gas produced at 750°—1000° C., finding in the gas, ethylene, propylene and a compound C_4H_6 which gave a crystalline tetrabromide, and in the tar, small amounts of the benzene homologues, but large amounts of naphthalene and some anthracene and chrysene. Tocher [49a] in the same year showed that in oil-gas produced at 500°—600° C., unsaturated hydrocarbons predominate in both the gas and the liquid formed, but at higher temperatures, the gaseous products are ethylene, methane and hydrogen.

Haber and his colleagues in 1896—97 [50a] stated that at 600°—800° C. hexane gives amylene, methane and benzene, with a little ethane

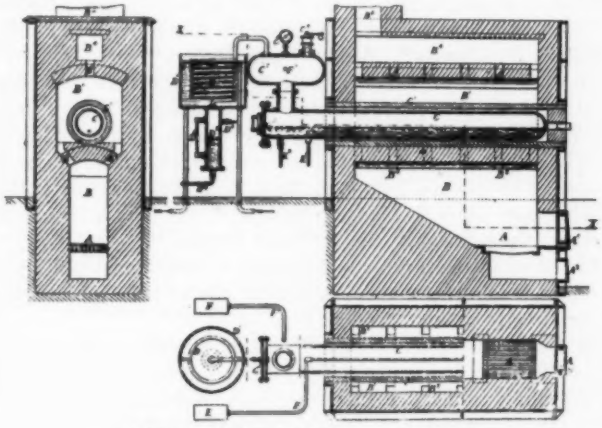


FIG. 1.—Redwood & Dewar Process.

and very little carbon and hydrogen, the olefine being always the bigger hydrocarbon. Trimethylethylene under the same conditions also gives benzene, therefore the benzene is not a direct product of hexane but is due to polymerization of acetylene. Benzene decomposed at 900° C. giving di-phenyl. At 900°—1000°C. the products are mainly methane, ethylene, hydrogen, carbon and tar.

Worstall and Burwell [57a] in 1897 decomposed crude heptane and octane at 900° C., obtaining the same class of products in both cases, i.e. gas, liquid hydrocarbons, tar and graphitic coke. The tar contained benzene, toluene, *o*–, *m*–, and *p*– xylenes, naphthalene, anthracene, phenanthrene and chrysene, with

unchanged heptane or octane, but no paraffins, naphthenes or acetylenes. They stated that at bright-red heat all hydrocarbons of the formula C_nH_{2n+2} gave the same products.

Zaloziecki [59a] in the same year found that petroleums heated in a sealed tube to not over 250° C. undergo intramolecular changes, i.e. isomerization of the hydrocarbons other than those of the paraffin series.

Pamflow [60a] obtained aromatic hydrocarbons from petroleum by passing it through a coiled tube at a temperature below that required for making oil-gas, and Boleg [60a] showed that by distilling hydrocarbons under 3—6 atmospheres pressure, the yield of light products is increased.

During this period several patents were registered for the production of aromatic hydrocarbons from petroleum and petroleum residues by Hlawaty and Friedmann [23], Dvorkovitz [24], Smith [26], Young [27], Dvorkovitz [29], Meikle [31], and Meffert [38].

The processes of Meikle and Meffert are the first in which is mentioned the use of steam in the retorts along with oil, although the subject had been investigated previously by Coquillion and Henrivaux [42a]. Several patents also were taken out for the manufacture of oil-gas and lighter products from petroleum by Laing [33], Yeadon and Adgie [32], Laing [35], Horsfall [39], the Soc. Internationale de Procédés A. Siegle [50], Siegle [51], and Ragosin [54].

In the meantime Engler and his pupils had commenced a series of researches on the origin of petroleum, some of the work of which bears directly on pyrogenesis.

In 1893, Engler and Singer [45a] obtained solid paraffin of m.p. 49°—51° C. by the dry distillation of fish oil, and in 1897 Engler [54a], by distilling animal fats under pressure, obtained oils containing little nitrogen which were however of light gravity and low boiling-point, and did not account for the oils of high gravity, molecular weight and boiling-point found in petroleum.

He proposed to ascribe the production of these higher compounds to the gradual polymerization of the lower ones, and gave instances of small increases of specific gravity on standing.

In the same year, along with Lehmann [55a], he examined the products of the distillation of fish oil under pressure, identifying the olefines from hexylene to nonylene, paraffins, benzene, toluene, metaxylene, mesitylene and pseudo-cumene, whilst the presence of naphthenes was not conclusively proved. In another paper he showed, in conjunction with Jezioranski, Grüning and Schneider, that the residues from the distillation of petroleum boiling above 200° C., decomposed on heating in open vessels or under pressure,

giving the lower members of the paraffin and olefine series from C_6 to C_{10}, along with aromatic hydrocarbons and some naphthenes, but when heated *in vacuo* distilled without decomposition. Later in 1906 Engler and Rosner [74a] examined the gas produced in the cracking of Baku crude oil, finding it to consist mainly of methane, ethane, hydrogen, and unsaturated hydrocarbons.

Krämer and Spilker [62a] in 1900 gave the results of distilling Baku residues at 450° C. under 20 atmospheres pressure, light oils being formed, and in 1901 Edeleanu [62b] obtained aromatic hydrocarbons by superheating certain fractions from Rumanian crude oil, while Singer [62c] in 1903—1904 showed that with Rumanian petroleum cracking takes place at as low a temperature as 200°—300° C.

Ipatiev, in 1904, [63a] stated that in the distillation of petroleum under pressure, at the higher pressures the evolved gases become continually poorer in hydrogen, in spite of the higher temperatures required to maintain the higher pressures. The pressures employed in his work were from 120—340 atmospheres.

Collie in 1906 [71a] submitted ethylene to the action of a silent electric discharge obtaining a liquid which was a mixture of high-boiling hydrocarbons, with hydrogen remaining; while Jackson and Lawrie [73a] submitted acetylene to a high-frequency discharge obtaining a solid polymer of benzene which on heating gave methane, hydrogen and a volatile oil. In the same year Pring and Hutton [73a] stated that carbon and hydrogen united directly at 1850° C., methane and acetylene being formed.

Bone and Coward in 1908 [73a], working on the thermal decomposition of methane, ethane, ethylene and acetylene, refuted this statement and stated that at high temperatures only methane was formed. They also stated that although acetylene is the principal product of the decomposition of ethylene at low temperatures yet Lewes's equation [45a] is wrong, but that when acetylene is the principal product in the decomposition, there is always a marked secondary formation of aromatic hydrocarbons. Above 800° C. they supposed the primary effect to be the elimination of hydrogen with a simultaneous loosening or dissolution of the bond, giving rise to residues such as $\cdot CH_2 \cdot$, $: CH_2$ and $\vdots\ CH_2$, which however can only have a fugitive existence, and may subsequently (*a*) form $H_2C \cdot CH_2$, $H_2C : CH_2$ and $HC : CH$, (*b*) break down directly to carbon and hydrogen, or (*c*) be directly hydrogenized. A study of this paper in detail is well worth the time spent on it.

In 1910 Pring [61a] repeated the experiments of Pring and Hutton [73a] showing that carbon and hydrogen combined at all temperatures

above 1100° C. Above 1550° C. the percentage of methane begins to increase with temperature, and that above this temperature acetylene is decomposed to ethylene and methane.

Later, in 1911 Pring and Fairlie [61a] showed that in addition to methane and acetylene the formation of ethylene has been detected between 1200°—1400° C.

The use of catalysts.—In 1897 Sabatier and Senderens showed that if ethylene is passed at 300° C. over finely-divided nickel (made by reducing the oxide by heating in a current of hydrogen, and cooling in the same atmosphere), the issuing gas is mainly methane with 10—50 % of hydrogen, and at lower temperatures ethane is also formed. This peculiar property of finely-divided nickel and other metals was further investigated by these two scientists, and they showed in 1899 [61a] that by passing acetylene and hydrogen over finely-divided nickel, copper, iron or cobalt at moderately low temperatures, liquid hydrocarbons containing paraffins, olefines and aromatic hydrocarbons are formed, together with ethylene and ethane, the proportion of liquid products formed increasing with the temperature, and that an increase in the proportion of acetylene used increased the amount of benzene formed. Later they showed that when a mixture of ethylene and hydrogen was passed over finely-divided metals, similar products were formed. The same reaction was tried with platinum black with similar results, but spongy platinum was found not to be so reactive. They also showed that by varying the ratios of the gaseous hydrocarbons and the hydrogen the character of the liquid products could be changed. In 1905 [70a] they showed that at 160° C. benzene is hydrogenized by catalysts such as finely-divided nickel, etc., to cyclo-hexane, and that by passing cyclo-hexane over the same materials at 270°—280° C. it is reduced to benzene. The results of this work of Sabatier and Senderens excited the interest of other investigators, and in 1906 Ipatiev [72a] showed that ethylene when heated in a sealed tube at 400°—450° C. with finely-divided iron or copper readily polymerized, but at higher temperatures much methane, ethane and hydrogen are also formed, whilst, in presence of an excess of hydrogen, methane is the chief product.

When benzene derivatives are heated with dry hydrogen in presence of iron, copper or aluminium at 400°—450° C, Ipatiev stated that the benzene nucleus is not hydrogenized even at very high pressures (220 atmospheres), but that in presence of nickel it is slowly, but quantitatively, converted into cyclo-hexane.

In 1907 Kuznetzov [76a] stated that methane, ethane, ethylene

and acetylene are decomposed into their elements by passing over red hot finely-divided aluminium.

Mailhe [79a] in 1908 used finely-divided nickel, copper, iron or cobalt to bring about molecular cleavages.

Above 250° C. benzene was decomposed to carbon and methane and cyclo-hexane to benzene and methane.

In 1910, Ostromislenski and Buryanads [80a], working on Russian crude petroleum, showed that in presence of nickel at 600°—700° C. it breaks down completely to gas and coke, the gas consisting of 72—75 % of hydrogen, and the remainder being saturated paraffins, while naphtha in presence of iron-gauze breaks down to acetylene, which polymerizes to benzene.

Ipatiev and Dowgelewitsch in 1911 [80b], found that hexane and cyclo-hexane, passed through an iron tube heated to 650°—700° C., were decomposed, the reaction being accelerated by aluminium. The products of the reaction contained paraffins, olefines and hydrogen, but no aromatic hydrocarbons. Under high pressure, hexane decomposed with explosive violence, but cyclo-hexane under high pressure, and in presence of alumina, gave olefines, cyclo-paraffins and benzene derivatives, the formation of methyl-cyclo-pentane taking place only in presence of catalysts. In the same year Zelinski [80c] showed that palladium black reduces cyclo-hexane and methyl cyclo-hexane to benzene and hydrogen, and toluene and hydrogen respectively. The reaction commences at 170° C., and proceeds rapidly at 200°—300° C. No di-hydro or tetra-hydro-derivatives were formed. At 100°—110° C. in presence of hydrogen, the reverse action takes place. Hexane, cyclo-pentane and methyl cyclo-pentane are not acted on below 300° C. Cyclo-hexene, prepared from cyclo-hexanol, acts more energetically, giving benzene and hydrogen, while a cyclo-hexene obtained from iodo-cyclo-hexane gave benzene and a new cyclo-hexene. Copper, silver and magnesium were inactive under these conditions.

In 1911—1912 Ubbelohde, St. Philippide and Woronin [93a] studied the effect of fuller's earth, unburned kaolin, ignited alumina and nickel on petroleum, in a current of pure hydrogen or nitrogen. Decomposition giving rise to lighter distillates, than by heating the oil alone, occurred with alumina at 350° C., nickel at 300° C., kaolin at 250° C., and fuller's earth at 250° C., while in the same year Engler [93b] discussed the influence of catalysts such as clay, silicious earth, sand, fuller's earth and metallic oxides on the formation of petroleum from fats at high temperatures and pressures.

Smith and Lewcock in 1912 [94a] described the influence of temperature and continued heat on the formation of di-phenyl from

benzene. The benzene was passed through an iron tube heated from 600°—800° C., and various oxides were used as catalysts, but they soon became coated with carbon. Yields up to 59% of di-phenyl were obtained.

In 1912 also Zelinski and Herzenstein [96a] showed that by passing a mixture of cyclo-hexane and ethyl-cyclo-pentane over palladium black at 300° C. till no further hydrogen was evolved, the methyl-cyclo-pentane could be recovered unchanged, the cyclo-hexane being converted to benzene, thus showing selective catalysis; similar results were obtained with fractions from Baku naphtha.

Jones in 1915 [115a] heated various hydrogenated aromatic hydrocarbons in presence of porous porcelain; at 500° C., cyclo-hexane gave benzene and higher olefines, ethane, methane, ethylene, hydrogen, traces of acetylene and unchanged cyclo-hexane. At 530° C. methyl-cyclo-hexane gave similar products to cyclo-hexane. At 420° C. 1 : 4 di-hydronaphthalene gave naphthalene, hydrogen, methane, and traces of higher olefines and ethylene, and at 530° C. 1 : 2 : 3 : 4 tetrahydronaphthalene gave naphthalene, benzene, higher olefines, methane, ethane, ethylene and hydrogen.

In the same year Tchitchibabin [122a] stated that the effect of heat on acetylene in the presence of different catalysts consists of three principal processes: (1) Local decomposition of the acetylene into carbon and hydrogen, accompanied by polymerization into aromatic hydrocarbons; (2) Condensation to solid hydrocarbons, similar to cuprene: (3) Hydrogenation of acetylene and aromatic hydrocarbons with formation of hydrocarbons of the paraffin, olefine and cyclic series.

Zelinski in 1915 [130a] stated that in cracking petroleum for aromatic hydrocarbons improved yields of benzene and toluene are obtained by using alumina and titanium oxide as catalysts.

Slater 1916 [131a] found that while several surface-catalysts increased, silica retarded the velocity of decomposition of methane.

This scientific investigation of the effects of catalysts on the decomposition of hydrocarbons naturally reacted on the technical side of the subject, and since 1906 many processes for the production of light spirits by the action of catalysts have been patented.

Day in 1906 [26] proposed to distil oils under pressure, in the presence of hydrogen or an absorbable hydrocarbon, and a catalyst, such as palladium black or spongy platinum, in order to produce light saturated oils.

In 1908 Sabatier [29] took out his first patent on the treatment of oil in presence of catalysts, in order to obtain from heavy oils or lamp oils a spirit boiling below 150° C. The vapours of the

heavy oils are passed over finely-divided metals at 400° C. or dull red heat, and the product from this reaction, which consists mainly of unsaturated hydrocarbons, is then hydrogenated in presence of finely-divided metals at 150°—300° C.

Phillips and Bulteel in 1909 [43] patented a process for the production of light oils from heavier mineral oils by heating in presence of hydrogen or hydrogenized gases and a catalyst such as powdered nickel, a rapid gyratory motion being imparted to the mixture of oil-gas and catalyst as it entered the retort.

Hausman and Pilat 1909 [44] specified the use of oxides, peroxides, or salts of metals capable of acting as oxygen-carriers, in the decomposition of petroleum or hydrocarbon vapours.

Planes, Ltd., and Thompson 1913 [68] proposed to crack petroleum or other heavy hydrocarbons by heating in a cracking still with a catalyst such as finely-divided nickel, and hydrogen or purified water-gas, and with violent agitation during the operation. The distillation is effected at about 300° C., and under a pressure of 5–100 lbs. per sq. in. It is mentioned that the heavy hydrocarbon is first purified from asphalt, sulphur, and other catalytic poisons.

Franke 1913 [73] also specified the use of pyrophoric metals such as iron, nickel, chromium, and platinum, together with hydrogen given off from the oil during cracking.

Gross 1913 [75] proposed the use of metallic oxides, hydroxides or basic salts in the preparation of isoprene by the pyrogenetic decomposition of turpentine, copper oxide being instanced as suitable.

Hall 1913 [76] took out a patent for the production of motor-spirit from heavy hydrocarbons by heating the vapours under pressure in the presence of a catalyst capable of affixing hydrogen, allowing the vapours to expand and deposit carbon, and then condensing them. The temperature specified is 600° C. upwards, pressure 5 atmospheres and the catalysts, metals such as nickel, cobalt, silver, palladium, chromium or manganese, or their oxides.

Holcgreber [79] in a patent of 1913, stated that benzene is obtained from the vapours of petroleum or its distillates by passing them, together with hydrogen, through a tube containing catalytic materials heated to 180°—300° C. Acetylene is said to be first formed and then polymerized to benzene. Suitable catalysts are iron, copper, zinc, aluminium, nickel, cobalt, silver and platinum or mixtures thereof.

The use of hydrogen and nickel as a catalyst for converting the unsaturated products from the cracking of oils into saturated aliphatic hydrocarbons was claimed in 1913 by Sommer [83] and also by the Steaua Romana Petroleum-Ges.[84] Valpy and Lucas

in 1913[94] patented a process in which a mixture of oil and steam is brought into contact with a heated catalyst, such as nickel or other metal or metallic oxide. The production of the catalysts was the subject of a further patent in 1914,[95] these being made by heating a powdered metallic oxide or mixture of oxides with organic compounds of the metal. In a later specification the uses of permanent gas partly saturated with ammonia gas is covered. The oil to be cracked is distilled in a separate still, and the vapours are passed through a cracking tube, packed with the catalyst, and heated to 550–600° C. The cracked vapours pass through fractionating, condensing and stripping plant. Part of the uncondensed gas now passes through an ammonia saturator under a slight pressure to the still, where it is sprayed over the surface of the oil. This helps to carry the oil vapour as fast as it is formed to the cracking tube, and incidentally reduces the temperature of distillation of the oil. It is claimed that a portion of the ammonia is dissociated, forming nascent hydrogen, which in the presence of the catalyst hydrogenizes a portion of the unsaturated hydrocarbons formed, and appears also to arrest the separation of carbon. The ammonia has yet a further action in that it tends to produce a sulphur-free spirit, even when an oil containing 5 to 6 per cent. of sulphur, such as Mexican oil, is employed. A commercial unit erected at Dagenham has been in intermittent use for the past two years, about 50 tons of oil having been run through it. The authors have had the pleasure of examining a sample of refined spirit produced in this plant which had been made about eighteen months, and found it completely free from the usual obnoxious polymerization products. It had a smell which was not so pronouncedly cracked as some of these spirits, a comparatively low unsaturated content, and was quite 'water-white.' The plant is very simple in action and is very easily controlled. A cracking plant to produce 2,000,000 gallons of spirit per year, including 'crackers,' distilling and refining plant, and gas producer plant for heating stills, crackers, etc., would cost about £50,000.

Sabatier and Mailhe, 1914[96], decomposed heavy hydrocarbons by passing them over a net-work of wires heated electrically from 500° C. to red heat, and subsequently converted the unsaturated compounds produced into saturated hydrocarbons by hydrogenation over finely-divided metals at 200°—300° C.

Hirschberg, 1914[96], proposed to use the voluminous chromium oxide obtained by calcining the chromium salts of volatile bases, such as ammonium chromate, as a catalyst for the conversion of heavy hydrocarbons into lighter hydrocarbons.

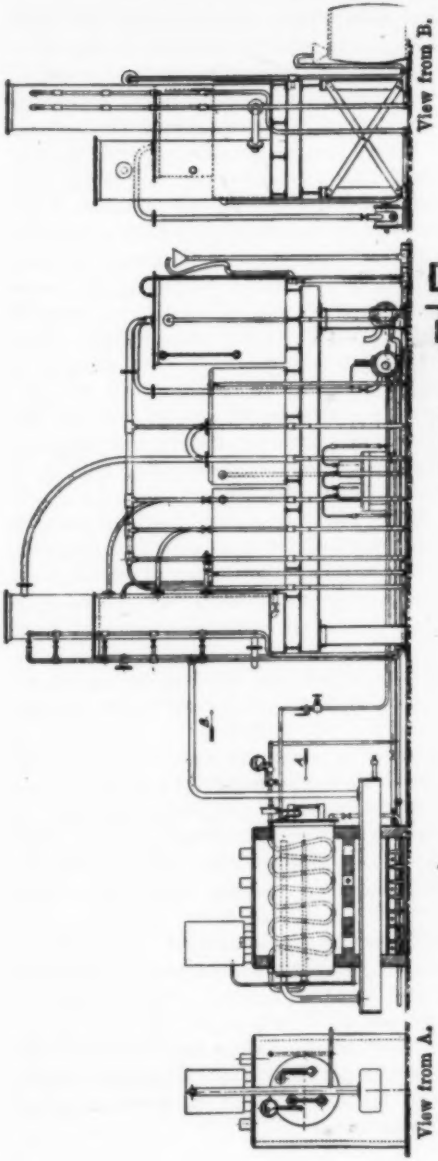


FIG. 2.—Lucas Oil-Cracking Plant.

White, 1914 [98], obtains light spirit from mineral oils and residues by bringing them in the liquid state, without steam or water, on to quicklime or quicklime containing carbon, at 400°—650° C. Herber, 1914 [111] proposed distilling oil mixed with lime in the presence of water or steam to produce lighter hydrocarbons. Porges and others, 1914 [100] used iron oxide or the oxide of another metal capable of forming several oxides as catalyst, passing over it oil-vapours and steam at 500°—600° C., the catalyst when exhausted being regenerated by heating in a current of air or oxygen.

Sabatier and Mailhe, 1914 [109], converted crude petroleum into volatile hydrocarbons boiling below 150° C., by passing it over a heated catalyst composed of finely-divided metals, or metallic oxides (iron oxide) or salts capable of reduction to metals, mixed with a neutral refractory substance free from silica (magnesia, alumina, graphite), and an agglutinant free from silica (glue, dextrine, starch). When the catalyst became coated with carbon, it was regenerated by a current of steam, and then reduced by hydrogen. In a further patent [116] the catalytic agent is maintained at a temperature of 300° C. by an electric current.

Higgins and Preston, 1914 [115], heat heavy hydrocarbons under a pressure, to such a temperature that the least volatile constituent is vaporised, and then the vapour either alone or mixed with hydrogen is passed through a catalytic medium, such as a mixture of nickel oxide and pumice stone, and condensed in contact with the medium.

Low, 1916 [122] converts high-boiling oils into low-boiling oils by spraying them by means of hydrogen against a heated plate, having a surface of catalytic material.

Action of metallic halides.—The well-known reaction of Friedel and Crafts has formed the basis for a number of experiments on the decomposition of hydrocarbons. In 1877 Abel [8] patented a process in which hydrocarbons are treated with aluminium chloride (anhydrous) or other metallic chlorides at 100°—600° C., whereby petroleum is converted into light oils, and naphthalene into benzene and toluene.

In 1881 Gustavson [21a] treated hydrocarbons obtained by fractionating American ligroïn or Caucasian kerosene by dissolving in them aluminium bromide, and then passing a stream of hydrobromic acid through. The liquid separates into two layers, the lower, being always approximately the same, points to the formula $AlBr_3.C_4H_8$. This layer is decomposed at 120° C., giving gaseous hydrocarbons. The upper layer consists of unsaturated hydrocarbons and simple homologues.

Heusler [82a], in 1896, stated that unsaturated hydrocarbons are polymerized to saturated hydrocarbons by aluminium chloride, and at the same time sulphur is removed, and in 1902 Aschan [84a] showed that at low temperatures olefines are polymerized to naphthenes in the presence of anhydrous aluminium chloride.

Engler [85a], in 1910, in his researches on the composition of lubricating oils, states that amylene heated under pressure gives methane and hydrogen, but with anhydrous aluminium chloride it gives a natural lubricating oil, which on further heating gives paraffins, naphthenes and olefines, while solid paraffins give liquid paraffins and olefines under heat and pressure.

Ipatiev and Routala, 1913 [86a], showed that if ethylene is heated with anhydrous zinc chloride under a pressure of 20 atmospheres polymerization takes place at 275° C., olefines, paraffins and naphthenes being formed. In the presence of anhydrous aluminium chloride, polymerization takes place at a lower temperature, but less naphthenes are formed.

In the same year a patent was taken out by the Continental Caoutchouc and Gutta Percha Co. [87] for the production of mineral oils of low boiling-point from those of high-boiling point by heating the high-boiling fraction with a catalyst such as aluminium chloride, with or without mercuric, ferric, vanadium, or other chloride or with aluminium in a stream of dry hydrochloric acid gas. In the same year a patent on similar lines was granted to Gray [88], who cracked oils by heating them with anhydrous aluminium chloride, ferric chloride or other metallic chloride at temperatures not higher than the final boiling-point of the product desired. For naphtha the temperature was 325°—350° F., and for kerosene 500°—600° F., the cracking being effected in a still fitted with stirring blades.

In 1914 and 1915, McAfee [114, 116 & 117a] took out several patents for the preparation of motor-spirits from heavy oils, claiming large yields of water-white, sweet-smelling, saturated compounds of low boiling points. The dried heavy oil is distilled with anhydrous aluminium chloride in a still fitted with a stirrer, at a temperature of 500°—550° F. (260°—288° C.).

It is difficult to see on what grounds these latter patents were obtained, as the process, chemical agent, and conditions had been specially and specifically mentioned in prior patents.

Recent work on the thermal decomposition of hydrocarbons.—Kharitchkov in 1910 [89a] subjected residues boiling above 270° C. from Baku and Grozni oil to cracking, and obtained respectively 25 % and 18·9 % of products boiling below 270° C. in each case, together with a very fluid residue resembling solar oil. In 1911

Ipatiev [98a] showed that by heating ethylene and isobutylene in an iron tube under a pressure of 70 atmospheres, rapid polymerization took place at 380°—400° C. From ethylene he obtained saturated paraffins ranging from isopentane to nonane, amylene and hexylene; and naphthenes from nono-naphthene to pentadecanaphthene. The fractions boiling above 250° C. were poorer in hydrogen than polymethylene compounds. In the case of isobutylene, hydrocarbons were formed which reacted with nitrating acid and potassium permanganate, but were insoluble in concentrated sulphuric acid (sp. gr. 1·84), and were probably aromatic hydrocarbons. Ethylene does not polymerize at 600° C. under atmospheric pressure. He suggests that the ethylene hydrocarbons are probably produced by polymerization of ethylene itself or from polymethylene compounds by fission of the ring; and saturated hydrocarbons by the hydrogenation of closed-chain hydrocarbons with fission of the ring; or by fission of the side chain from polymethylene nuclei.

Meyer and Tanzen in 1912 [98b] passed equal volumes of acetylene and hydrogen through two tubes consecutively, the first heated to 640°—650° C. and the second to about 800° C. In the tar formed, they identified phenanthrene, acenaphthene, styrene and *n*-hexylene.

Staudinger, Endle and Herold in 1913 [99a] by passing isoprene through a tube heated to 750° C. obtained 50 % of tar containing benzene, toluene, naphthalene, methylnaphthalene, anthracene, chrysene and also butadiene, methane and carbon; at 400° C. the isoprene was mainly unattacked, but small quantities of terpenes and amylene were obtained; from 600°—700° C. the product was mostly unsaturated hydrocarbons; from 700°—750° C., aromatic hydrocarbons began to be formed, and above 800° C. the product consisted mainly of aromatic hydrocarbons.

Jones and Wheeler in 1914 [103a] by distilling bituminous coal *in vacuo* at temperatures up to 430° C., obtained about 6·5 % of tar, which consisted of about 50 % volatile below 300° C., and a pitch boiling above 300° C. The oils volatile below 300° C. consisted of ethylenic hydrocarbons of indeterminate composition, for the most part richer in carbon than the mono-olefines (C_nH_{2n}) equal to 40—50 %; naphthenes and liquid paraffins, the former in excess, about 40 %; aromatic hydrocarbons about 7 % (apparently homologues of naphthalene, naphthalene itself not being detected), and a small quantity of solid paraffin. Benzene, anthracene, carbon bi-sulphide and solid aromatic hydrocarbons were absent.

Sernagiotto in the same year [104a], by treating methyl alcohol with phosphorous pentachloride, obtained olefines and naphthenes, i.e. compounds of the general formula C_nH_{2n}, but no ethylene, which is strong evidence of the fugitive existence of nascent radicles : CH_2, as suggested by Bone and Coward [70a].

Rittman, 1914 [103a & 106a], discusses the theory of equilibria involved in the cracking of oils.

Petroni, 1914 [107a], subjected crude Bustenari petroleum and its products to destructive distillation obtaining aromatic hydrocarbons. In the same year Meyer and Fricke [111a] found *m*– and *p*–xylene, α and β methyl-naphthalene and hydro derivatives of naphthalene in tar obtained from acetylene, in all 23 compounds present in ordinary coal tar were detected.

In 1915 a large amount of experimental work was carried out, but it is worthy of note that the source of the large portion of it was the United States ; for obvious reasons, the investigations of European workers having been directed into other channels. This work of the American investigators, although of great interest from a technical standpoint has not advanced the real knowledge of pyrogenesis to any great extent, being too empirical.

Whitaker and Alexander [113a] showed that temperature and rate of flow determine the properties of oil gas made from kerosene, higher temperatures and lower rates of flow increasing the rate of decomposition, and that proportion of free hydrogen formed.

Brooks and others [114a & 119a] showed that the olefine content of gasoline prepared from heavy hydrocarbons decreased as pressure of preparation increased, up to a maximum of 200 lbs. per sq. in., and then remained constant ; and that the percentage of gasoline increased to 280 lbs. per sq. in. and then decreased. The temperature of working was 600°—700° C. Working at 100 lbs. pressure, aromatic hydrocarbons were formed which they suggested were derived from petroleum hydrocarbons containing the phenyl group.

Bjerregaard [115a] passed crude petroleum and kerosene through an iron coil at pressures ranging from 275—1400 lbs. per sq. in. and temperatures from 340°—440° C. and then expanded into vessels kept at 20—30 lbs. per sq. in. Yields of low-boiling oils depended on rate of feed and pressure. At these low temperatures no aromatic hydrocarbons were found.

Rittman, Twomey and Egloff [116a] stated that the percentage of aromatic hydrocarbons in cracked oil could be estimated from the specific gravity of the fractions obtained when following specified directions.

Sterne [118a] examined the condensate from carburetted water-gas

finding it to consist of 75·9 % paraffins, 1·6 % olefines and 22·5 % of aromatic hydrocarbons.

Ellis and Wells [120a] in discussing the properties of gasoline made by cracking kerosene, pay attention to the high specific gravity, iodine absorption and refractive index and find that the polymer deposited on standing decomposes on distillation, even under a vacuum of 6—10 m.m., stating also that the polymerized products react with sulphur and sulphur chlorides, and that the gas produced gives with chlorine a liquid product.

Rittman, Byron and Egloff [121a] subjected aromatic hydrocarbons to cracking in the vapour phase under various conditions and found that general reaction may be indicated as follows :—higher benzene homologues → lower homologues → benzene → (diphenyl) → naphthalene → anthracene; the reverse reactions being negligible.

Ostromislenski [122a] stated that the pyrogenetic decomposition of homologues of di-pentane at 500°—600° C. yields homologues of isoprene, and that of saturated hydrocarbons and such as contain one double linking, yields erythrene, but not its homologues. Erythrene may be obtained from almost any hydrocarbon containing not fewer than four carbon atoms in the molecule.

In 1916 Friedmann [149a] showed that very pure normal octane heated in a sealed tube at 280° C. gives fractions boiling at 118°—127° C. Whitaker and Leslie [154a], following up Whitaker and Alexander's work [112a], studied the effect of the addition of hydrogen in making oil-gas, the concentrations being approximately $H_2 : 1$ of oil-gas and $2H_2 : 1$ oil-gas. The absorption of hydrogen is greater the higher the concentration, the higher the temperature, and the lower the rate of oil feed. The formation of methane is greater the higher the temperature.

Davies [155a] obtains gasoline practically free from unsaturated hydrocarbons from high-boiling petroleum oil by mixing the vaporized oil with superheated steam, and passing the mixture under pressure through tubular cracking apparatus packed with iron or steel shavings. The best conditions for experiment were found to be: pressure = 100 lbs. per sq. in., 10 lbs. of steam per one gallon of oil, steam superheated to at least 600° C. and cracking temperature 650°—675° C.

Zanetti [158a] subjected the propane (97 %)-butane (3 %) fraction from natural gas to cracking. At atmospheric pressure and up to 750° C., no aromatic hydrocarbons were obtained, but ethylene, butylene, etc., and hydrogen, the percentage of hydrogen being greater the higher the temperature. The unsaturated bodies

rose to a maximum at 750° C., and then decreased, benzene and toluene being found in the tar produced. Above 750° C. nickel and iron gauze inhibited the production of aromatic hydrocarbons, and favoured the production of carbon and hydrogen.

Brooks and Humphrey[143a] stated that benzene homologues are present in the high-boiling distillates of petroleum, basing their conclusions on cracking experiments carried out on Jennings and Oklahoma residues at temperatures not exceeding 420° C., and pressures not exceeding 100 lbs. per sq. in., in which they obtained small quantities of benzene homologues, also on the fact that Oklahoma oil heated with aluminium-chloride gave the same results, as did a synthetic phenyl-paraffin, made by condensing pure benzene with chlorinated paraffin wax in presence of aluminium-chloride; this on cracking gave benzene homologues, whereas paraffin itself did not give them. They claim that the temperatures used were too low to admit of the decomposition of hydrocarbons to acetylene with subsequent polymerization.

The work of Rittman, Twomey and Egloff[132a, 136a, 137a, 138a, 139a, 140a, 141a, 144a & 145a,] may be here conveniently classed together as having a bearing on the much-lauded Rittman vapour-phase cracking-process. Most of this work is relative to the conditions governing the production of aromatic hydrocarbons from petroleum. They show that the maximum production of benzene takes place when the production of toluene and xylene have decreased, i.e. at higher temperatures, and that at the same time naphthalene begins to be produced, arguing from this that naphthalene is formed by the decomposition of monocyclic bodies. At ordinary pressures, higher temperatures were required for the production of aromatic hydrocarbons than when under increased pressure, but even at low temperatures, i.e. 450°—600° C., some aromatic hydrocarbons are produced. Under pressures of 11—14 atmospheres, and temperatures from 600°—650° C., alkyl and alkylene derivatives of naphthalene give benzene and toluene, their formation being assumed to take place (1) by direct decomposition of methyl naphthalene; (2) by formation and subsequent decomposition of xylenes; (3) by synthesis from acetylene and allylene, the three reactions occurring either successively or simultaneously. Paraffin wax at atmospheric pressure and a temperature of 500° C. gave no aromatic hydrocarbons, but at 150 lbs. per sq. in. and a temperature of 600° C., appreciable yields of benzene, toluene and xylene were obtained, as well as liquid paraffins. Kerosene was subjected to the action of various

catalysts in the liquid-vapour phase, yields of cracked oils from the various catalysts being given.

Vignon [146a] distilled coal at 400°, 600°, 850°, 1000°, and 1200° C., and analysed the gases produced. Unsaturated hydrocarbons (ethylene, acetylene, etc.) are all distilled below 600° C., and are absent above this temperature. Methane and paraffins are very abundant up to 800° C., but then disappear: from 800°—1000° C., hydrogen predominates, but then falls off, and at the highest temperature carbon monoxide is found.

De Montmollin [147a] examined the "ethylene-petrol" formed by the action of phosphoric acid on ethylene, finding it to be a complex mixture of hydrocarbons, mainly polymethylene (cyclohexane homologues) together with unsaturated and saturated aliphatic hydrocarbons and aromatic hydrocarbons. Di-isopropyl (b.p. 58°—59° C.), di-methyl di-ethyl methane (b.p. 86°—87° C.) hexahydrometaxylene, and hexahydroparaxylene were isolated in a state of purity, and hexahydrocumene, hexahydrocymene, decanaphthene, dodecanaphthene and tetradecanaphthene were identified.

Oil-gas produced in cracking solar oil for motor-spirit, when passed through sulphuric or phosphoric acids, is polymerized, giving a mixture of liquid hydrocarbons; this product was examined by one of the authors in 1913 and found to consist of a mixture of polymethylene hydrocarbons, together with unsaturated hydrocarbons of the terpene or polyterpene series, which had pronounced siccative properties. It is hoped that an opportunity will arise for a further examination of this product.

Fischer [148a] treated naphthalene with 4 % of powdered aluminium chloride in a sealed tube for 3 hours at 330° C. About 40 % was converted into liquid hydrocarbons which analysis showed to have a composition intermediate between naphthalene and dihydronaphthalene.

Gurvitch [149a] treated freshly rectified amylene with floridin, the amylene being polymerized to di-amylene; carbon and alumina also affected the polymerization.

Recent patents on oil cracking.—The demand for volatile hydrocarbons for use as fuel in internal-combustion engines in late years, and the question of obtaining an increased production by the utilisation of fractions from crude petroleum of otherwise less value, has undoubtedly stimulated the activities of engineers and chemists in finding a solution of the problem, and over 60 patents with this end in view have been taken out since 1906.

Cowper-Coles in 1906 [85] was apparently the first inventor who

worked specially for a product adapted for use in internal-combustion engines, the method of production being to pass paraffin oil vapours through a series of small tubes heated to about 1700° F. (926° C.).

In 1908 Noad and Townsend[49] proposed to decompose oil and water in liquid form in the presence of each other and of highly heated iron in the form of scrap or the like, claim being made that the iron acted as catalytic agent. This patent was taken over by the New Oil Refining Process, and was followed by several others under these names in 1911 and following years [50, 51, 52, 53], in which claims were made for other packings in the retorts, and for temperatures of 1000—1200° F. (538°—649° C.). In the process as worked, the retorts were horizontal iron tubes about 12 ft. long and 9 in. in diameter, and 9 tubes were built in one battery. These retorts were packed with iron turnings rolled into the form of cartridges, fitting loosely into the tubes to facilitate removal. The retorts were heated by oil or gas burners, the gas for the latter being produced in the process, and the temperature about 600° C., was kept under recorded pyrometric control. The oil and water were fed into the retorts by separate pipes in the proportion of about four parts of oil to one part of water. On dropping into the retorts they were instantly vaporised, and the vapours thus formed were quickly removed from the sphere of action by means of an exhauster, passing first through a dephlegmator where the heavier products were condensed, and then to a water-cooled condenser, where the main fraction of the cracked oil was collected. The gas, still charged with light spirit, was passed through scrubbers to recover these bodies, and finally into a gasholder for use as fuel in the plant. The condensed cracked oil and spirit-laden scrubber-oil were passed through topping stills to remove all spirit, and were then mixed with the heavy condensates from the first dephlegmator to be returned through the retorts. Solar oil was the crude material used in the plant, and also as scrubber oil, the quantity used in the scrubbers each day being so arranged that it was equivalent to the quantity required in the converters next day. The spirit from the topping still was refined with sulphuric acid and alkali, and then steam-distilled through dephlegmators, giving a water-white motor-spirit, a solvent or paint spirit with flash-point over 73° F. and a residue suitable for varnish, rubber substitute, etc. The yields of finished products obtained from the original solar oil employed were :—Motor-spirit = 40 % : paint or solvent spirit = 13 % : varnish substitute = 13 % : gas = 30 % : carbon and loss = 4 %.

In this process the spirit produced had the inherent defects, and also the good qualities, of cracked spirits, but difficulties were encountered in the working on a large scale, and after some months of operation the process was finally abandoned.

In 1908 Testelin and Renard [41] patented a process in which petroleum is sprayed into a coil heated to 400°—450° C. under a pressure of 5 atmospheres by a steam injector, and then the vapours thus formed are passed through a red hot coil filled with burnt clay.

Wassmer, 1909,[44] subjected oil-vapours to the action of an electrically-heated conductor, so as to decompose them, whilst Adams, 1910,[46] cracked kerosene and similar oils by bringing them into contact with an incandescent electric heater, the oil being heated as far as possible by direct contact. Burke in 1911 [47] distilled heavy petroleum at low pressure, and condensed it at a pressure of 700 grm. to 85 kilos per sq. cm. Leffer in 1912 [53, 57 & 67] converts heavy hydrocarbons into light hydrocarbons by distilling under pressure of an inert gas at temperatures not exceeding 410° C.; the pressure used is 10—11 atmospheres and mixed vapours from the still may be further decomposed by passing through a chamber heated by steam or electrically.

Greenstreet [55, 66 & 120] passes heavy hydrocarbon oils mixed with steam by an atomizer through a continuous coil of pipe free from obstructions, about 100 ft. long and 1½ in. diameter, kept at cherry-red temperature, the oil and steam being supplied at 50 and 100 lbs. per sq. in. respectively. The products are led through fractional condensers, the temperature of the last one being just above 100° C., and the light vapours passing from this are condensed. The coil becomes coated internally with a smooth layer of magnetic oxide.

Lamplough [58] proposes to convert heavy hydrocarbons into light hydrocarbons by bringing the heavier oil, together with water or steam, into contact with nickel in a retort which is maintained at a dull red heat or thereabouts, more or less pressure being maintained in the retort, and 20—60 parts of water are used to 100 parts of oil. He claims that he has found that nickel has the valuable property of facilitating the conversion into light hydrocarbons, and that it maintains its surface clean and active not requiring such frequent cleaning as iron.

In this process Lamplough used an iron coil which had inside it a fairly close-fitting rod of nickel, which metal was considered to facilitate the conversion. At the same time the vapours were exposed to a larger surface of iron than of nickel, and it seems

probable that this influence would be in ratio to the surface exposed, and since metallic nickel, as distinct from reduced nickel, has no catalytic action in the true sense of the word, probably more of the cracking effect is due to the iron than the nickel.

One of the authors some years ago carried out comparative experiments using an iron tube packed with (1) iron (2) nickel and (3) quartz, but could find no difference in action whatever, an inert material such as quartz giving as large a conversion as either nickel or iron. No difference either could be found between the products in either experiment.

Ellis [60] was granted a patent for the cracking of heavy oils by injecting them through nozzles into a chamber filled with fire-brick, alumina, or other refractory material, and at the same

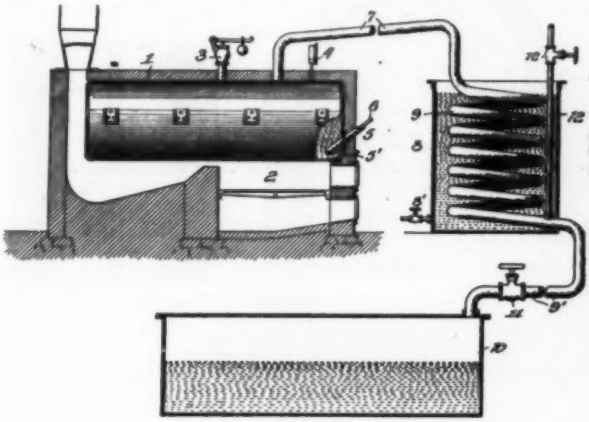


FIG. 3.—Burton Plant.

time injecting sufficient air for the combustion of a portion of the oil. The working pressure was 30—50 lbs. per sq. in. and the refractory material was coated with a layer of catalytic material.

Turner [61] passed oils, with water, through primary coils, at 60 lbs. pressure and at 400°—800° F., then passing the resulting vapours under pressure through secondary coils at temperatures from 1000°—1400° F. and finally into vessels of larger diameter to cause tarry and carbonaceous matters to be deposited. The vapours were cooled under ordinary pressure.

In The Standard Oil Co. (Burton) process [62, 101, 113 & 117] petroleum residues are distilled for the production of low-boiling hydrocarbons of the paraffin series at a temperature of 650°—850° F.,

the whole plant being maintained at a pressure of 4—5 atmospheres by means of valves placed at the outlet of the condenser. This process is apparently being worked to a large extent in the United States, but it is difficult to see on what grounds the patent has been granted. Distillation under pressure was practised by Young [3], but he did not condense under pressure, whereas Redwood and Dewar [20] both distilled and condensed under pressure, just as is claimed by the Burton process; with the exception that in 1889 there was not the demand for motor-spirit, and so the aim of the originators of the process was the increased production of kerosene. The identical apparatus devised by Redwood and

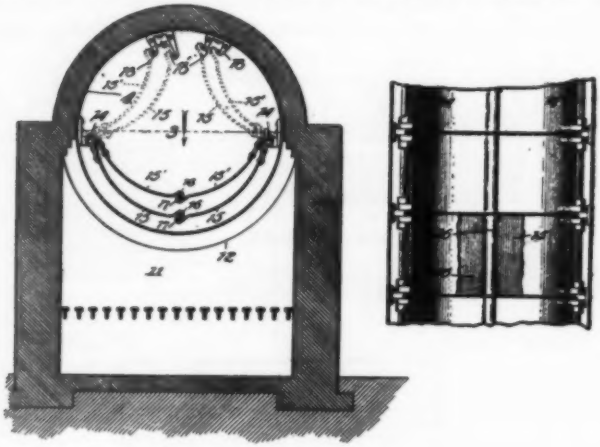


FIG. 4.—Burton Plant.

Dewar would do the same work, in exactly the same way, that the Burton process is doing at the present day.

Renard [66] in 1913 proposed to convert petroleum and other hydrocarbons into products of lower boiling-points by forcing them in the liquid state through a coil of tubing, the first part of which is kept at a temperature above the boiling point of the petroleum, while the second part is cooled, a pressure in excess of the vapour-pressure of the oil being maintained throughout the coil. The temperature maintained is from 400°—450° C., and the pressure is 40—50 atmospheres.

Von Groeling [71] distilled and cracked hydrocarbons by passing the vapours from a still through externally-heated cracking tubes, where they meet a descending stream of hydrocarbons. The

operation is conducted under slight pressure and at temperatures from 350°—500° C.

Moeller and Wolterick [77] converted crude or heavy oils into light oils by mixing their vapours with highly superheated steam (at 700°—800° C.) of substantially atmospheric pressure and passing the mixture over coke at dull red heat (600°—800° C.).

Hall [78, 87, 89, 92, 102, 105, 119 & 128] has been one of our most prolific inventors in the line with which we are dealing, and his process, modified from time to time as experience has been gained, is one, probably the most successful, of those being worked. It is hardly necessary for me to describe this process fully, as less than two years ago the inventor himself gave you a full description. Briefly, however, in the process as at present worked, the oil to be treated is passed through a continuous coil of about 600 ft. of cold-drawn tubing of 1 in. internal diameter, at temperatures and pressures which vary according to the desired product. The oil fed in at the cooler end of the retort is gradually heated and vaporised, the speed of the vapours being about 5000—6000 ft. in the latter portion of the coil, and where the temperature is highest. At the exit, the vapours are suddenly expanded into a tube of much larger diameter, down to atmospheric pressure. Here, an appreciable rise in temperature is experienced without external aid, due partly to transformation of the kinetic energy of the high velocity of the gases into heat, and partly to the disruption of the molecules of the oil. It is at this point that most of the cracking takes place, and a little graphitic carbon is formed. The vapours now pass through a series of dephlegmators, built on the Raschig principle. In the first of these, a little soft spongy carbon and pitch separate out, in the second a heavy residue free from pitch, and in the third one, a very light mobile residue. The vapours, cooled now to about 100° C., pass to compressors, which having already expanded the gas on exit from the converter tubes down to atmospheric pressure, now compress the wet vapours, which are cooled and stored under a pressure of 50—75 lbs. per sq. in.

A peculiar reaction has been noticed in these compressors when working for motor-spirit. As a rule, when gases are compressed, the temperature rises, but in the case of these gases, the temperature falls slightly after compression, which fall can only be caused by chemical combination, or polymerization of some of the lighter hydrocarbons, as it is well known that some of the hydrocarbons produced in cracking oil polymerize very readily even at ordinary temperatures and pressures. By re-running the residues from the second and third dephlegmators, yields of 70 % of motor-

spirit from the original oil used have been obtained. In working for motor-spirit, the temperature at the exit of the tubes is about 550°—600° C., a temperature which requires varying between these limits according to the oil being cracked, but when once the optimum temperature for any particular oil has been decided, this temperature can be most rigidly adhered to, variations of plus or minus 5° C. being the extremes over periods of several hours working. This complete control of the temperature is a very important consideration in a process of thermal decomposition, as, at the temperatures employed, the thermal coefficient is very high, and comparatively small variations give rise to very divergent results. This is a point, by the way, to which many inventors have failed to pay sufficient attention. The rate of feed of oil to the tubes is also very carefully regulated by means of meters, being checked to plus or minus 5 % of the feed per hour.

Hall's plant, with very small alterations, is eminently adapted for the production of aromatic hydrocarbons from petroleum, an installation consisting of eight converters with the necessary compliment of dephlegmators, compressors, condensers and tanks having worked on these lines daily for about eleven months with complete success, a spirit having been produced in good yields containing up to benzene = 18·5 %, toluene = 17·5 %, xylenes = 6·0 %, which is very easily refined, the refined products containing only traces of paraffin or naphthenes, e.g. from 1 to 2 % on the finished product. When working for aromatic hydrocarbons, the temperatures and pressures employed are necessarily higher than when working for motor-spirit, being respectively 750° C. and 105—110 lbs. per sq. in., but these temperatures and pressures are as easily controlled as when working at the lower ones. It might be argued that when working with tubes of this diameter and under these severe conditions of cracking, there is a liability of the tubes becoming choked with carbon. This difficulty was certainly encountered at first, but has been overcome, and it is now quite common for a nest of tubes to run over 250 hours without cleaning, and then only a few of the tubes require to be replaced by clean ones, and the nest can be restarted immediately. The high speed at which the vapours pass through the tubes causes a scouring action, which carries any carbon formed through to the expansion-tubes and dephlegmators, whence it is very easily removed. A fairly large amount of gas of high calorific value (= 1350 B.T.U.), and having a distinct commercial value is necessarily formed when cracking for aromatic hydrocarbons. Incidentally it may be mentioned that the aromatic hydrocarbons

contained in the spirit produced can be very easily estimated by simple modifications of the James and Coleman tests, determinations by which agree very closely with the results obtained by fractionation to pure products. In the higher boiling portions of the spirit, i.e. those boiling between 150°—250° C., naphthalene is formed, and has been isolated in a pure state and identified, while it is very probable that its derivatives are also present.

Graefe and Walther [85] transformed heavy hydrocarbons into lighter ones by distilling under a pressure of 20—30 atmospheres in an autoclave. This, however, hardly seems to have much prospect of success on a large scale.

Shedlock and The Optime Motor Spirit Syndicate,[91] for the production of motor-spirit from heavy oils, emulsify the heavy oils with water by means of resin, soap or other emulsifying agent, and then heat the emulsion under pressure at about 500°—900° F. in presence of iron or steel shavings or other catalyst. The oil before emulsification is treated to remove sulphur and pitch. We understand that this process is being worked in this country, but do not know with what success.

Gray [94] passes oil through a bath of molten metal kept at a high enough temperature to cause cracking.

Fenchelle and Perkin [100] have patented a process in which heavy hydrocarbons are converted into lighter hydrocarbons, by heating them in the liquid state to 500°—600° C. under a pressure of 50—60 atmospheres. The liquid, still under pressure, is then cooled to about 150° C., and allowed to escape at a lower pressure into a chamber, in which the lower hydrocarbons vaporise simultaneously. The invention is applicable to liquefied hydrocarbons such as naphthalene and paraffin wax.

In this process it is claimed that by treating in the liquid phase in this manner very little carbon is deposited, and from all accounts a very fair amount of success has been met with in the experimental stage.

By Bacon and Clark [109] petroleum hydrocarbons having a boiling point of about 250° C. and upwards are decomposed and distilled under a pressure of 100—300 lbs. per sq. in., the heat being applied at such a rate as to give a minimum yield of 18 % of gasoline boiling below 150° C.

Snelling [110 and 128a] states that by heating low-grade crude oils, aliphatic oils, paraffin wax, rod wax, kerosene, lubricating oils, fuel oils, tarry still residues, etc., in a closed vessel to such a temperature that the vapours evolved produce an added pressure of preferably 600—800 lbs. per sq. in., a product resembling high-

grade Oklahoma crude oil is obtained, which on distillation yields gasoline up to 20 % and kerosene up to 40 %. The still is preferably filled to $\frac{1}{3}$—$\frac{1}{2}$ of its cubic capacity.

Marks and Iroline Co. [120] use the same process as Snelling, reference being directed to his patent.

Bacon, Brooks and Clarke [121] convert petroleum oils boiling above 250° C. into products boiling below 200° C., by submitting them to a combined distilling and cracking operation, in a vertical tubular retort at a temperature of 350°—500° C. and pressure of 60—300 lbs. per sq. in. The particles of tar and coke produced sink to the bottom of the retort and are removed.

Dubbs [122] mixes petroleum with water under pressure and then vaporises the mixture under pressure. The pressure is then relieved, and the vaporised mixture discharged into a heated chamber in the form of fine spray. The resulting vapours are subsequently condensed.

Washburn and New Process Oil Co. [124] transform petroleum products of specific gravity ·794—·901 into products of specific gravity not exceeding ·777, by heating with water in a retort at 340°—510° C., and condensing the vapours under a pressure of 3—5 atmospheres, which is maintained both within the retort and condenser. In this case also it is difficult to understand how a patent has been obtained in face of the prior patents of Young [8], Redwood and Dewar [9] and the numerous patents of the Standard Oil Co.

Hall [125 & 126] obtains lower boiling distillates from heavy oils, oil residues and bitumens by distillation at 475°—490° C., in vertical retorts, mixed with equal or larger quantities of coke.

Palmer [130] increases the yield of volatile hydrocarbons from petroleum residues, by digesting them under pressure of the evolved vapour (60—400 lbs. per sq. in.) at a temperature above 200° C., but below that at which substantial carbonisation takes place, and without the addition of steam, the heating being continued until the greater portion of the residue is converted into more volatile compounds, which are separated when the pressure is relieved.

Wells [131] decomposes heavy oil vapours by conducting them into a bath of molten lead, which is heated to about 480°—540° C. and is violently agitated by mechanical means.

The Rittman process for the manufacture of gasoline and benzene-toluene from petroleum and other hydrocarbons, which has been so largely boomed in America, has been recently granted letters patent in England [132]. The investigations which led to this discovery, and its large-scale development were under the

direct auspices of the U.S. Bureau of Mines, which tends to show how much importance is attached to this subject in that country. It was no doubt also influenced by the abnormal price which had to be paid for toluene about 12 months ago. As finally adapted for commercial purposes, the benzene-toluene plant consists of six furnaces, each heated by 22 gas burners and containing 2 rows of 5 vertical cracking tubes (11½ ft. long and 8 in. diameter). To each tube is fitted a separate condenser and the oil supply for each tube is separate. Carbon deposited on the walls of the converter tubes is removed by wiping-chains attached spirally

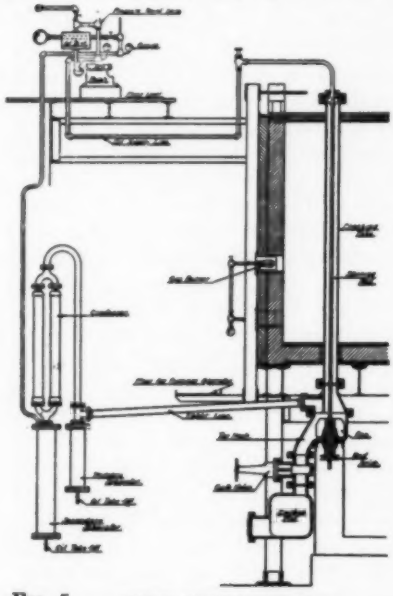


FIG. 5. — BUTTNER CRACKING PROCESS.

to a rotating rod passing up the centre of the tube, and is collected in special carbon pots by means of scrapers at the bottom. The cleaning device requires to be removed and cleansed every few days.

For the preparation of benzene-toluene the rate of feed to each tube is 15 gallons per hour and for gasoline 30 gallons per hour). Temperatures of about 700° C. and pressures of about 150 lbs. per sq. in. are employed. The reactions are found to be practically independent of the kind of oil used, although solvent naphthas and light oil distillates from coal tar and water-gas tars give

greater yields of benzene-toluene than is obtained from petroleum products, and are easier to handle.

A large amount of gas of high calorific value (1000—1400 B.T.O. per cub. ft.) is obtained, more than sufficient as fuel when the plant is run for benzene-toluene, but not sufficient for this purpose when running for gasoline.

The following yield from petroleums are claimed in the benzene-toluene process:—benzene 6—8 %, toluene 6—8 %, xylenes 4—6 %, gasoline 6—8 %, creosote oil and pitch (including higher aromatic hydrocarbons and lubricating oil) 25—30 %, carbon 3—5 % and gas 45—60% of the original oil, and when working for gasoline:—25—30 % of gasoline with residuum above 150° C.=70—73 % which is available for re-running.

The cost of installation based on a unit of 4 tubes is £1,146 per tube, which includes building and equipment, but not the cost of storage-tanks or apparatus for treatment of products.

It has long been known that aromatic hydrocarbons can be produced from certain types of petroleum, a process having been patented as early as 1860 for their recovery from oil-gas made from petroleum, but Rittman claims that it has never before been demonstrated that they can be produced in considerable quantities from any type of oil. In the early part of 1915, however, they were being produced in this country by the Hall process, which, if not prior to the Rittman process (which is very probable), was at least abreast with it, for it was not until much later that in this country at least we began to hear so much of the "new" discovery emanating from America. Studying the plant itself from the published photographs and sketches, it appears to be rather a cumbersome affair, several of the details striking one as not being quite sound. The tubes used in the process are most unwieldy, and it is difficult to understand how the vapours passing through can be at all evenly heated, in spite of the central cleaning rod which gives the retort an annular form. Oil-vapours are bad conductors of heat, and tubes of an inch diameter are more correct theoretically from this standpoint at least.

It is claimed that absolute command over the operating conditions is possible by causing the reactions to take place in the gaseous or vapour-phase. This term gaseous or vapour-phase has been used as a hook upon which to hang a whole series of claims, whereas numerous prior inventors have worked on, and specifically mentioned, that condition. One fails to see how "absolute command over the operating conditions" can be claimed, when such crude methods of temperature-measurements as the naked

eye, supplemented by periodic checks by pyrometers, are employed. It is well known that temperature-variations of an amount impossible to recognize by the naked eye, cause enormous differences in the character of the products evolved at these high temperatures, and these variations cannot be averaged up as to their effects. No cracking process can be completely successful, unless equable temperature-conditions are maintained. The design of the furnace containing the retorts, can hardly be conceived to aid in this matter, since wide differences must necessarily exist in different parts of it. The operation of changing the cleaning rods must take some time, as this portion of the apparatus cannot be easily handled while hot, and thus the operations cannot be nearly continuous. Intermittent cooling and heating of the brickwork and tubes must also be detrimental to them. It might be mentioned here that in the New Oil Refining Process particular attention was paid to the question of cleaning the tubes, which were arranged in such a way that a whole battery of 9 tubes could be cleaned while hot, the entire operation from shutting off of oil and water to starting again taking about 20 minutes. Another point which strikes one is: how is the stuffing-box of the stirrer rod kept tight at 700° C. and 150 lbs. pressure?

The cost of the installation appears almost prohibitive, taking a unit plant consisting of 60 tubes, the cost would be £68,760 and this on the benzene-toluene process would handle about 18,000 American gallons of oil per day. With the Hall process a plant capable of handling 10,000 American gallons of oil per day would cost about £12,000.

The analysis of the spirits produced in the Rittman process as to aromatic hydrocarbon content is carried out in a most empirical manner, and depends on the specific gravity of fractions obtained by two fractionations through a 5 in. Hempel column, the second series on which the determination is made being cut at 95°, 120° and 150° C. It was then assumed that other bodies present with the aromatic hydrocarbons possessed an approximative value as below:—

Temperature of Cut.	Specific Gravity of Aromatic Hydrocarbon.	Specific Gravity of Non-aromatic Hydrocarbon.
95° C.	0·880	0·720
120° C.	0·871	0·730
150° C.	0·869	0·760

and a calculation from the determined specific gravity taking the above figures was used. In the decomposition of petroleum at varying temperatures it is well known that the proportions of

constituents in the products vary very considerably, and if more than two classes of bodies are present, this assumption as to the gravity of the non-aromatic constituents cannot possibly hold good, being open to variation within wide limits. The benzene-toluene spirit produced in the Rittman process contains considerable quantities of non-aromatic bodies unattacked by strong sulphuric acid, and for the production of trinitrotoluene from the toluene fraction, special methods have to be devised. The spirit produced by the Hall process on the other hand contains only minute traces of non-aromatic bodies unattacked by strong sulphuric acid, and the toluene produced is as easily nitrated as coal-tar toluene.

Part II.—*General Considerations.*

By A. E. Dunstan and F. B. Thole.

Although the origin of the term cracking is due to petroleum practice, yet the investigation of the pyro-analysis and pyro-synthesis of hydrocarbons goes back to the days of the great chemist, John Dalton [1a], who in 1809 decomposed methane and ethylene by means of electric sparks. It might possibly be urged that this decomposition is scarcely analogous to the cracking of a heavy hydrocarbon, but in point of fact the complexity of this latter process is so great and the multiplicity of its products are so confusing that the study of the subject must necessarily proceed from the starting point of the simplest possible reactions. Only in this way can one throw light on one of the most intricate problems that ever confronted the chemist.

To the mind of Berthelot [13a, 14a, 15a] the pyrogenetic decomposition of hydrocarbons resolved itself into simple polymerization or else condensation with loss of hydrogen. Moreover he contended that each change was reversible, so that at any particular temperature an equilibrium could be established between a complex series of decomposing, polymerizing or condensing hydrocarbons, together with free hydrogen and carbon. In the case of the four simple hydrocarbons Berthelot considered that the following reactions took place:—

Methane	$2CH_4 = C_2H_2 + 3H_2$
	$2CH_4 = C_2H_6 + H_2$
Ethane	$C_2H_6 = C_2H_4 + H_2$
	$2C_2H_6 = 2CH_4 + C_2H_4 + H_2$
Ethylene	$C_2H_4 = C_2H_2 + H_2$
	$2C_2H_4 = C_2H_6 + C_2H_2$

It will be seen that Berthelot ascribed to acetylene a most important rôle in the pyrogenetic phenomena as it always appears

either as an intermediate or a final product. It is a well-known precursor of the aromatic hydrocarbons, and its chemically reactive nature fits it to be the "générateur fondamentel des cardures pyrogenées." When acetylene was heated to a dull red heat, Berthelot obtained from it benzene, styrolene, naphthalene and retene:—$3C_2H_2 = C_6H_6$ benzene : $4C_2H_2 = C_8H_8$ styrolene : $9C_2H_2 = C_{18}H_{18}$ retene.* At a bright red heat it was decomposed into its elements.

Whilst Berthelot's views must be regarded as crude and insufficiently based on experimental evidence, yet the credit of putting forward for the first time a well-articulated theory of pyrogenesis is undoubtedly his.

Work on the lines laid down by Berthelot was vigorously pursued. The acetylene theory was violently attacked on the ground that it was difficult or impossible to isolate that hydrocarbon in the products of pyrogenesis. Thorpe and Young [21a], Armstrong and Miller [35a], and Haber [59a] considered that the first steps were the elimination of hydrogen and the production of olefines and methane, without any intermediate production of acetylene:—

$$2C_6H_6 = C_{12}H_{10} + H_2$$

diphenyl.

$$CH_3(CH_2)_4\,CH_3 = CH_3(CH_2)_2\,CH : CH_2 + CH_4$$

hexane. amylene.

A paper of capital importance was contributed in 1908 by Bone and Coward [79a] on the thermal decomposition of methane, ethane, ethylene and acetylene. Their main conclusions may be briefly summarized as follows:—(1) Methane is exceedingly stable. It decomposes almost exclusively into its elements, and this decomposition is in all probability reversible at all temperatures. The dissociation is in the main a surface phenomenon at moderate temperatures. (2) The thermal decomposition of the other three hydrocarbons is not so obviously a surface effect; it originates and is propagated in the body of the gas. (3) Acetylene is produced when ethylene suffers decomposition, but is not formed during the heating of ethane or methane. (4) At comparatively low temperatures acetylene polymerizes quite easily, yielding cyclic hydrocarbons, mainly of the aromatic type. Consequently whenever ethylene is a primary product of pyrogenesis, acetylene will appear intermediately, polymerizing at once into benzene and its congeners. The optimum temperature for this polymerization is between 600° and 700°; at 1000° there is little evidence of this

* It requires a profound application of scientific imagination to visualize this nono-molecular reaction.

phenomenon. (5) Acetylene and ethylene combine with hydrogen at moderate temperatures yielding ethane. This reaction, however, ceases to be effective at 1000°. (6) One of the principal factors in operation at temperatures of 800° and higher is the direct hydrogenation of "nascent radicles" such as CH ⋮ , CH_2 : , CH_3 · , for which molecular fragments must be postulated a free although momentary existence during the dissolution process. This assumption undoubtedly accounts for the presence of the large amounts of methane which are always produced during any cracking operation.* (7) In the cases of ethane and ethylene, it may be supposed that the primary effect of high temperature is to bring about an elimination of hydrogen, with a simultaneous loosening of the linkings between the carbon atoms, giving rise to the residues CH_2: and CH⋮. These residues can only have a fugitive existence and may (*a*) unite to form $CH_3 : CH_2$ or CH ⋮ CH; (*b*) decompose yielding carbon and hydrogen; or (*c*) be reduced to methane. Thus

$$\left.\begin{matrix}CH_3 \cdot CH_3\\ \text{ethane}\end{matrix}\right\} \rightarrow 2CH_2: + H_2 \rightarrow \begin{cases} C_2H_4 + H_2 & (a)\\ 2C + 3H_2 & (b)\\ + H_2 = 2CH_4 & (c)\end{cases}$$

$$\left.\begin{matrix}CH_2 : CH_2\\ \text{ethylene}\end{matrix}\right\} \rightarrow 2CH: + H_2 \rightarrow \begin{cases} C_2H_2 + H_2 & (a)\\ 2C + 2H_2 & (b)\\ + 2H_2 = 2CH_4 & (c)\end{cases}$$

(8) In the case of acetylene, the main primary effect is probably polymerization, but the possibilities of dissolution must also be borne in mind :—

$$\left.\begin{matrix}CH \vdots CH\\ \text{acetylene}\end{matrix}\right\} \rightarrow 2CH: \rightarrow \begin{cases} 2C + H_2 & (a)\\ + 3H_2 = 2CH_4 & (b)\end{cases}$$

(9) Berthelot's theory of the attainment of equilibrium between dissolution and recombination is not borne out by experimental evidence.

The Thermochemistry of some Pyrogenic Reactions.—It will readily be appreciated that the majority of the reactions which proceed during pyrogenesis are either unknown or else complicated by side and consecutive changes. It is therefore very difficult to trace the distribution of energy during cracking. Taking some of the simplest operations described by Bone and Coward, it is possible to discover by means of well-recognised thermochemical data, the concomitant energy-relationships :—

A. $C + 2H_2 = CH_4 + x$ calories.

Intrinsic Energy :—

$O + O = -21{,}750 + x$ calories

$x = 21{,}750$ calories.

* Bone's theory is of interest in considering the possibilities of hydrogenation during cracking. Apparently much of the hydrogen would be utilised in the generation of methane.

Thus there will be, for gram molecular quantities, an evolution of 21,750 calories, i.e. the reaction is exothermic.

B. $3C_2H_2 = C_6H_6 + x$ calories

$3(+47{,}770) = 12{,}510 + x$ calories

$x = 130{,}800.$

The reaction is exothermic.

C. $C_3H_6 = C_2H_4 + H_2 + x$ calories

$-28{,}560 = 2710 + O + x$ calories

$x = -31{,}270$ calories.

The reaction is endothermic.

D. $C_2H_6 = 2C + 3H_2 + x$ calories

$-28{,}560 = O + O + x$ calories

$x = -28{,}560.$

The reaction is endothermic.

E. $C_2H_6 + H_2 = 2CH_4 + x$ calories

$-28{,}560 + O = -2 \times 21{,}750 + x$ calories

$x = 14{,}940$ calories.

The reaction is exothermic.

F. $C_3H_8 = C_2H_4 + CH_4 + x$ calories

propane

$-35{,}110 = 2{,}710 + (-21{,}750) + x$ calories

$x = -16{,}070$ calories.

The reaction is endothermic.

G. $C_2H_2 + 3H_2 = 2CH_4 + x$ calories

$47{,}770 + O = -2 \times 21{,}750 + x$ calories

$x = 91{,}270$ calories.

The reaction is exothermic.

H. $C_2H_4 = C_2H_2 + H_2 + x$ calories

$2710 = 47{,}770 + O + x$ calories

$x = -45{,}860.$

The reaction is endothermic.

J. $C_2H_4 + 2H_2 = 2CH_4 + x$ calories.

$2710 + O = -2 \times 21{,}750 + x$ calories

$x = 46{,}210.$

The reaction is exothermic.

K. $C_2H_4 = 2C + 2H_2 + x$ calories

$2710 = O + O + x$ calories

$x = 2710.$

The reaction is exothermic.

L. $C_6H_{14} = C_5H_{10} + CH_4 + x$ calories

hexane amylene

$-57{,}600 = -12{,}500 + (-18{,}900) + x$ calories

$x = -27{,}200.$

This typical cracking reaction is endothermic.

N. $2C_6H_6 = C_{12}H_{10} + H_2 + x$ calories
diphenyl
$2 \times 11{,}300 = 33{,}500 + 0 + x$ calories
$x = -10{,}900.$
The reaction is endothermic.

O. $C_6H_{12} = C_6H_{12} + 3H_2 + x$ cal.
hexahydrobenzene
$-46{,}600 = 4100 + 0 + x$ cal.
$x = -50{,}700.$
The reaction is endothermic.

It will be noticed that those reactions which proceed by absorption of hydrogen are in the main exothermic, i.e. the products formed have a less content of intrinsic energy than their generators, in other words, they are relatively more stable.

A genuine cracking process such as is exemplified in the equation:

$$C_2H_6 = CH_4 + C_2H_4$$

is endothermic seeing that in part, relatively unstable molecules (the olefines) are being formed. It must be borne in mind also that these unsaturated products have a proportionally greater heat of combustion.

e.g. ethane C_2H_6 possesses heat of combustion = 370,440 c.
less H_2 ,, ,, ,, = 68,357 c.
302,183 c.
ethylene C_2H_4 ,, ,, ,, = 333,350 c.
i.e. excess over $(C_2H_6 - H_2)$ ... ... = 31,167 c.

From the Nernst quotation:

$$Q = RT^2 \cdot \frac{d}{dt} \log_e K$$

where Q is the heat of reaction,
R the gas constant,
T the absolute temperature,
K the equilibrium constant,

It is possible to calculate the temperature-coefficient $\left(\frac{d}{dt} \log_e K\right)$ of the velocity of reaction.

In general the temperature-coefficient is surprisingly constant, for it has been found that for most chemical reactions the velocity is very approximately doubled for a rise of 10° C. To quote a few examples:—

Reaction.	Velocity constants.	Quotient for 10°.
$AsH_3 = As + 3H$	$K_{256} = 0{\cdot}00035$; $K_{267} = 0{\cdot}0084$	1·23
$H_2O_2 = H_2O + O$	$K_0 = 0{\cdot}0120$; $K_{10} = 0{\cdot}0180$	1·5
$2NO = N_2 + O_2$	$K_{280} = 39{\cdot}68$; $K_{1247} = 191800$	1·17
inversion of cane sugar.	$K_{25} = 0{\cdot}765$; $K_{35} = 35{\cdot}5$	3·6

There are certain consequences of changes of temperature and pressure on equilibrium which must be borne in mind.

Le Chatelier has enunciated a general law which may be stated as follows:—

When one or more of the factors determining an equilibrium is altered, the equilibrium becomes displaced in such a way as to neutralise, as far as may be, the effect of the change.

Thus, consider the change

$$C + 2H_2 = CH_4 + 21{,}750 \text{ c.}$$

Heat is set free during the synthesis of methane, consequently if heat is admitted to the system, the equilibrium is displaced in such a direction that heat is absorbed, i.e. the dissociation of methane sets in. Similar considerations from the point of view of pressure change will be discussed later.

The Influence of Temperature on Cracking.—It is evident from the work of Bone and Coward in particular, and of all previous workers in general, that at the highest possible temperatures there is complete dissolution of a hydrocarbon into its elements. In other words, chemical affinity ceases to act when the atomic vibrations reach a certain limiting value. This phenomenon holds good in some cases at quite low temperatures, as witness the dissociation of arsenic hydride and hydriodic acid.

The temperature at which cracking begins depends mainly on the molecular weight and the constitution of the oil; speaking broadly, the more complicated the molecule, the more readily it undergoes dissolution, and further, the more unsaturated and labile the compound, the more easily it disintegrates. It has been shown above that the velocities of chemical changes are profoundly affected by changes in temperature. It is, therefore, easily credible that the most extraordinary differences in the nature of the products may be observed if the working temperature is even slightly altered, for one particular reaction may be so damped or accelerated as to mask entirely the progress of other parallel or simultaneous changes.

The theorem of Berthelot and Thomson that a chemical reaction tends to proceed, giving rise to products that occasion the greatest development of heat, must always be borne in mind. This theorem

means that reactions are propagated of themselves if more stable bodies are formed under the conditions of temperature and pressure which obtain during the experiment. But it should be remembered that the changes which go on during cracking are not necessarily those which would spontaneously go forward to completion. Many exothermic reactions doubtless do go on to the end, but the endothermic processes, such as the pyroanalysis of ethane, $C_2H_6 = C_2H_4 + H_2 = 31{,}270$ calories, can be maintained only by the absorption of a large supply of energy.

Not only does alteration in temperature affect the speed of the various reactions but also most profoundly does it alter the nature of the products. In the majority of commercial cracking systems it has been found that whereas at moderate temperatures (*circa* 500°) the tendency is for the formation of a mixture of paraffins and olefines, at higher temperatures (*circa* 700°) the effect is the generation of aromatic compounds.

From the large number of experiments recorded in the tabular matter on pp. 97–112, it will be of interest to study a few examples.

The effect of temperature-changes on the velocity of the decomposition of ethane may be briefly summarised:—

Up to 675° decomposition is slow, six hours being needed to eliminate 98 % of the hydrocarbon.

At 800° the reaction was so rapid that five minutes sufficed to transform the same percentage.

At 1000° still less time was required, whilst at 1140°–1145° the gas barely survived a single passage through the tube.

Vignon [140a] distilled coal at various temperatures and analysed the gases produced:—at 400°–600° there were formed acetylene and ethylene; at 600°–800° methane and other paraffins; at 800°–1000° much hydrogen.

Staudinger [99a] and his co-workers heated isoprene to a variety of temperatures:—

At 400° the products were amylene, terpenes and unattacked isoprene; at 600°–700° the products were unsaturated hydrocarbons; at 700°–750° aromatic hydrocarbons appeared; at 750° the tar contained benzene, toluene, naphthalene, methyl naphthalene, anthracene and chrysene, whilst hydrogen, butadiene, methane and carbon were also produced; at 800° the products were entirely aromatic. Staudinger considers that the isoprene condenses to form hydroaromatic compounds, which ultimately at high temperature lose hydrogen, generating benzenoid hydrocarbons.

Zanetti [156a] cracked a mixture of 97 % propane and 3 % butane, derived from natural gas:—at 750°, there were formed in the main

ethylene, butylene and hydrogen. $C_3H_8 = C_2H_4 + [CH_2]$; $CH_2 + CH_2 = C_2H_4$; $C_4H_{10} = C_4H_6 + H_2$. Above 750°, benzene, toluene, and other aromatic bodies were found to be present. The higher the temperature, the greater was the proportion of free hydrogen. It is noteworthy that as Zanetti's material was low in molecular weight and high in stability a greater degree of temperature was needed for this cracking.

Rittman [121a, 192a, 136a, 137a, 182a, 140a, 141a, 144a, 145a], to whose credit much interesting work must be put, considers that "gasoline" formation begins at about 400°, and approaches a maximum at 500°–550°. The greatest content of aromatic hydrocarbons occurs between 650° and 700°. These optimum temperatures are naturally functions of the nature of the oil, the pressure, the size and shape of the reactive space and the rate of feed.

Rittman uses the Nernst formula to calculate the reaction velocities of a large number of possible and impossible changes at various temperatures. For example:—

		$K_{600°}$.	$K_{750°}$.	$K_{900°}$.
$C + 2H_2 = CH_4$	...	0·077	0·012	0·003.
$C_2H_6 = C_2H_4 + H_2$	...	0·0027	0·094	1·28.

Against this last result must be urged the objection that Bone and Coward found that ethylene is produced to a less and less extent as the temperature rises, the percentage of this gas after one minute being at 675°, 24; at 810°, 11; at 1000°, 7, and at 1140° nil.

Such reaction as $7C_{10}H_{14} = 10C_7H_8 + 9H_2$; $6C_7H_8 = 7C_6H_6 + 3H_2$; and $7C_8H_{10} = 8C_7H_8 + 3H_2$, which are quoted by Rittman, are frankly impossible from molecular kinetic considerations, for the last case pre-supposes that collision between seven similar molecules are occurring simultaneously. It is possible that Rittman is writing this equation as the sum total of a number of consecutive reactions, in which case the velocity constants calculated by him only represent the *slowest* in a series of several superimposed rates.

Ipatiev [69a, 69a] finds that cyclohexane is much more resistant to heat than the open-chain hexane. The increased stability of ring systems is, of course, well known, and in this connection it is interesting to note that the cracking process which is worked at the highest temperature, viz., cracking coal into coal gas, produces a tar which is prolific in compounds which contain complicated condensed rings. At 600–700° Ipatiev found that both hexane and its cyclic analogues yield olefinic, but no aromatic compounds. In the presence of alumina and under high pressures, cyclohexane at 500° gives rise to olefines, polymethylenes, benzene and saturated

polynuclear hydrocarbons. Some methylcyclopentane is also formed —an interesting example of the great stability of the five-membered ring. The same author found that ethylene [73a] and iso-butylene were capable of polymerizing at quite low temperatures (380–400°) when at 70 atmospheres pressure, producing paraffins, olefines and cycloparaffins, together with high-boiling products of an unsaturated nature.

R. Meyer [90a and 111a] repeated some of Berthelot's work, and in particular showed that acetylene at 640°, diluted with hydrogen gave a tar rich in light oils, but at high temperatures one abundant in hydrocarbons of very high molecular weight. He obtained products varying from benzene to fluorene and chrysene.

The cracking of petroleum with the object of producing aromatic hydrocarbons has come greatly to the front recently, and in particular in those countries where supplies of coal or coke-oven tar are relatively scanty. Lunge, the great authority on coal-tar, rather scoffs at such attempts to make benzene and its homologues, but he fails to realise that at times like these every possible source of new material for the manufacture of high explosives should be exploited.

The thermal decomposition of petroleum into aromatic compounds occurs at temperatures considerably in excess of those needed for simple cracking, and in consequence much more serious losses occur in the shape of carbon and fixed gases. Paraffin hydrocarbons at these temperatures are almost completely decomposed. The desired products are not the primary results of cracking; they are obtained from them by further decompositions and syntheses. Accompanying them are other characteristic bodies, usually classed under the heading of unsaturated hydrocarbons, but which are far more reactive than the simple olefines. Butadiene is a typical example of the compound, and it was identified by Berthelot, Armstrong and Miller, and Thorpe and Young. The presence of these highly active products renders the working up of the aromatic hydrocarbons a little difficult until experience shows how they may best be eliminated.

Summing up, therefore, the effects of temperature on petroleum distillates of the nature of solar oil it may be said that (1) Temperatures up to 500–600° yield in the main a mixture of olefines and paraffins; (2) Temperatures *circa* 700° yield a mixture of olefines, diolefines and aromatic hydrocarbons, with little paraffins; (3) Temperatures *circa* 1000° yield mainly permanent gases (much methane) and a tar similar to coal-tar, in that both contain aromatic hydrocarbons.

The effect of Pressure on Cracking.—Considering any reversible reaction, it is found that on increasing the pressure at constant temperature, the equilibrium is displaced in the direction in which the volume diminishes. This is but a special case of Le Chatelier's law, that when one or other of the factors which determine an equilibrium is altered, this equilibrium is displaced in such a way as to neutralise, as far as possible, the effect of the change.

This law must be borne in mind whenever any change in temperature or pressure is contemplated.

Again taking as an example the reaction—$C + 2H_2 = CH_4 + 18{,}900$ calories, it is obvious that since this change proceeds from left to right with a diminution of volume, the formation of methane will be accelerated by increase in pressure. Similarly, since this same reaction is exothermic, increase of temperature will retard the formation of methane.

In general terms, it will be seen that increased pressure favours synthesis or combination, whilst diminished pressure promotes analysis or dissociation. If cracking were merely a gas proposition, one would undoubtedly crack under a lowered pressure, and at high temperature, in other words adopt gas works practice.

A further point that must be borne in mind depends on the effect of pressure on concentration, for a reaction proceeds with a velocity depending on the concentration of the reacting substances and their products.

Consider the reaction :—$C_2H_6 = C_2H_4 + H_2$. If the hydrogen is maintained within the sphere of operation, the reaction will attain a position of equilibrium when certain limiting concentrations of the gases are reached ; addition of more hydrogen will bring about reduction of the ethylene until the balance is readjusted. Removal of hydrogen will cause the complete dissolution of the ethane.

The two equilibria discussed in this section are interesting in that they show how irreconcilable are the demands made by the chemist who desires to produce the maximum yield of light spirit, and the minimum of carbon, from a given oil. On the one hand, increasing pressure promotes the hydrogenation of carbon and other unsaturated compounds, whilst on the other hand, the primary dissolution of a paraffin into the lower olefine is inhibited.

On surveying the literature, it is found that the general effect of excessively high pressures is to bring about reactions at low temperatures, which otherwise would require much more drastic heating. These reactions are mainly in the nature of polymerizations, for Ipatiev obtained from ethylene at 400° and 70 atmospheres pressure a very wide range of complex hydrocarbons and Egloff and

Twomey [141a] similarly obtained aromatic compounds from paraffin wax at a lower temperature by employing a higher pressure.

It may therefore be concluded that high pressure favours complex-building and reduction. Some technical processes of the two-phase type makes use of high pressure to maintain the necessary cracking temperature.

Catalysis.—Moissan first noticed that when acetylene is brought into contact with a variety of freshly reduced metals, it decomposes with incandescence producing liquid hydrocarbons, among which is benzene. In 1899 Sabatier [61a] passed a mixture of acetylene and hydrogen over reduced nickel, and obtained a complete reduction to ethane. This reaction was considered by its eminent discoverer to be explicable on the ground that reduced nickel formed an unstable hydride, and this substance yields atomic or nascent hydrogen to the acetylene. The nickel can be regarded as a catalyst of hydrogenation, but it would be anticipated that this metal should be capable of combining with hydrogen already in a state of combination; in other words it should react as a catalyst of dehydrogenation, and in point of fact it does so. Many examples have already been given which show that at sufficiently high temperatures all hydrocarbons are decomposable into products of lower molecular weight. In the presence of catalysts this change can be accomplished at a lower temperature, and therefore with a greater degree of ease and less loss.

When acetylene is passed over reduced nickel at 250° C., carbon and hydrogen and liquid hydrocarbon result. These latter bodies on being hydrogenated over nickel at 200°–300° yield saturated paraffinoid and cyclo-paraffinoid products. Sabatier actually obtained from acetylene replicæ of Pennsylvanian, Baku and Galician petroleum, and somewhat boldly endeavoured to explain from his results the occurrence of natural oil on the assumption that beds of reduced metal exist in the terrestrial stratification.

Whilst the hydrogenation of such unsaturated hydrocarbons as are present in cracked oils offers the most attractive prospects, it must be borne in mind that (1) Catalysts are very readily poisoned by traces of sulphur-compounds, arsenic and the halogens; (2) excess of free hydrogen must be employed; (3) relatively low temperatures are needed. The activity of the catalysts is greatly reduced or even entirely inhibited at temperatures higher than 400°; (4) the best catalyst is nickel; cobalt and iron are much inferior, whilst copper begins to be effective at about 400°; and (5) a catalyst accelerates a reversible change in either sense of the reaction.

Various Catalysts.—In most cracking processes there will be some deposition of carbon. It is, therefore, of interest to observe any specific instance where carbon has been found beneficial catalytically.

Coke.—Bone and Coward point out that sugar charcoal promotes the reaction:—

$$C + 2H_2 = CH_4.$$

Smith and Lewcock [94a] find that coke accelerates the formation of diphenyl, and Slater similarly agrees that this catalyst is effective in the decomposition of methane.

Reduced Nickel.—Zanetti finds that this substance at high temperature inhibits the formation of aromatic hydrocarbons, but obviously the specific catalytic action of this element is inoperative except possibly as a catalyst of dehydrogenation. A similar result was observed by Ostromislenski [82a]. Ipatiev reduced benzene to cyclohexane, and showed the reversibility of the reaction. He also reduced ethylene to ethane, whilst, of course, Sabatier has accomplished a great number of such reactions.

Alumina and floridin.—These compounds have been used by Gurvitch [149a], and even at atmospheric temperature and pressure they possess the power of polymerizing amylene into diamylene. Ipatiev has also used alumina in the polymerization of ethylene to aromatic compounds.

Aluminium chloride and other anhydrous metallic haloids.—Humphrey [143a] converted various heavy petroleum residues into aromatic compounds, using aluminium chloride, and McAfee has patented a cracking process which depends on the same catalyst. Aluminium bromide has been used by Gustafson [81a]. Both Aschan [64a] and Ipatiev [98a] have polymerized olefines at relatively low temperatures in the same way. It should be borne in mind, however, that the free hydrogen haloids are quite energetic in polymerizing unsaturated hydrocarbons, so that it is not impossible that at least some of the activity of these metallic chlorides is due to hydrolytic formation of hydrogen chloride. This is borne out by the work of Egloff and Moore [144a]. Most chemists appear to regard the reactivity of aluminium chloride as being due to the formation of intermediate additive compounds, followed by their scission and the building up therefrom of new compounds.

Other Materials.—The iron tubes and retorts in which cracking proceeds, masses of metallic substance, shavings, blocks of metallic oxides, and the like have been used as catalysts. It is a very moot point whether any of these bodies exerts a specific action. In all probability their application depends on this general advantage of surface. Too much importance can hardly be assigned to

these quasi-catalytic effects due to surface-action. To quote only a few: there are the Welsbach mantle, the Bone-Court furnace, the contact process for sulphuric acid, and colloidal palladium hydrosols. Whether the surface acts purely physically as an adsorptive medium, or whether there are formed loosely-held complexes, is entirely a matter of opinion.

It must always be remembered that a catalyst in a reversible reaction equally catalyses the reverse change. For example, consider the formation of methane from its elements:—

$$C+2H_2=CH_4$$

Whatever catalyses the synthesis of methane will also catalyse its analysis. At any given temperature, a condition of equilibrium tends to obtain, and the catalyst simply accelerates the establishment of this condition.

The Mechanism of Pyrogenesis.—The opinion that Berthelot so ably sets forth relating to the formation of condensation or polymerization products appears diametrically opposed to any final views of the mechanism of cracking, since simplification and dissolution are the objects of this operation. Yet the opposition is of degree rather than of kind, for Berthelot made use of temperatures and conditions which lead to pyrosynthesis following upon pyroanalysis.

The swing of the pendulum led to the theory of nascent radicles, which was handled so skilfully by Bone and Coward, and which from the point of view of the coal-tar chemist appears so inevitable. But is it necessary to postulate so profound a dissolution in the customary cracking operation? Without doubt at temperatures approaching 1000° C. such a radical break-up of organic molecules is possible and probable, but are we to contemplate this inter-atomic disruption at temperatures so low as 500°?

The answer to this question is both in the negative and the affirmative. Given a definite hydrocarbon with which to start, and conditions of temperature and pressure not drastic, there is no reason to go further than the views of Thorp and Young and of Haber, who suggest that a simple scission takes place:—

$$C_6H_{14} = C_5H_{10} + CH_4.$$

This theory is supported by the work of Ipatiev, Norton and Andrews [37a] and Zanetti. It must be recognised, however, that to accomplish this step in a heterogeneous mixture would be impossible, since each compound needs an optimum temperature for this simple cleavage.

Consider the next step, predicating that the chosen paraffin has split into olefine and simple paraffin. The latter will probably not

crack further, since its stability is greater than that of its generator. What will be the fate of the olefine? A diligent search among the literature will show that at quite moderate temperatures and in the presence of all sorts of catalysts and quasi-catalysts, olefines are extremely reactive. For example, Ipatiev from isobutylene obtained paraffins, olefines and cyclo-paraffins. Aschan at low temperature found that polymerization to cyclo-paraffins took place, whilst Gurvitch obtained diamylene from the simple olefine. On the other hand, Engler discovered profound decomposition into carbon, hydrogen and methanes. Quite a number of recent patents propose to make isoprene and erythrene by the thermal decomposition of unsaturated hydrocarbons, and here we have yet another possibility of pyrosynthesis. What is the mechanism of this variety of reactions? Engler [85a] considers that the olefines condense with elimination of hydrogen, to form an artificial lubricating oil.

Heating this body, there result paraffins, naphthenes and unsaturated compounds. Further, that olefines yield polyolefines, which are degraded in quite a similar manner by the effect of heat. It is a well-known fact that most simple olefines, even with sulphuric acid treatment, yield the bi-molecular polymer, e.g., amylene produces di-amylene.

Assume then that the olefines as a preliminary stage polymerize or condense with elimination of hydrogen. The next step in the argument is due to Ostromislenski, who last year showed that dipentene yields isoprene when heated to 400°–600°

$$C_{10}H_{16}=2C_5H_8$$

and dihexane produces dimethylerythrene. Further, the higher olefines break down, as shown in the equation :—

$$CH_2:CH\cdot CH_2CH_2R \rightarrow CH_2:CH-CH:CH_2+RH$$

Erythrene appears to be an almost universal product in the cracking of petroleum.—It was isolated by Berthelot, Armstrong and Miller, Noyes and Mory [85a 85b], Norton and Andrews, and has been observed by the present authors in an investigation dealing with the compounds present in spirit produced by the Hall process. Curiously enough isoprene itself has never been identified in the products from petroleum. Apparently one must have a complex diolefine as a primary product.

A slight variation from the above theory is due to Ipatiev, who suggests that ethylene itself may be a starting point for the formation of higher olefines by a process of polymerization. It is unlikely, however, that this is more than a contributory factor to the main primary scission at low temperatures. More plausible is

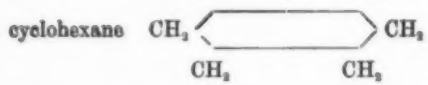
the same author's view that polymethylenes are a primary product after the preliminary break up. Thus

heptane $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$

$\downarrow$

hexylene $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 : CH_2 + CH_4$

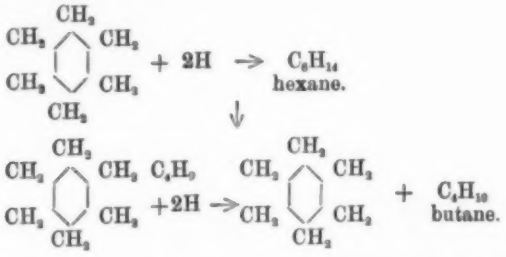
$\downarrow$

cyclohexane 

In this case it must be borne in mind that ring formation is unlikely unless five or more carbon atoms are present in the homocatenary hydrocarbon, which is the starting out material.

Ipatiev's view, therefore, is by no means incompatible with the theory outlined above, and it leads to interesting consequences.

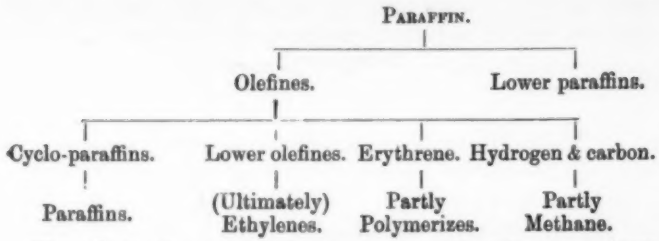
Given the presence of free hydrogen, the scission of this cyclo-paraffin ring would lead to the production of saturated homocatenary hydrocarbons, and further, the side chains of cyclo-paraffin might well split off, yielding paraffin:—



What a large range of polymerization is possible may be gathered from the summary given by Lebedev [150a]. This chemist recognises five types of product:—

Via ethylene to styrolene, $R \cdot CH : CH_2$
and to stilbene, $R \cdot CH : CH \cdot R$;
Via acetylene to benzene and its homologues;
Via allene to cyclobutene; and
Via erythrene to cyclohexane.

The following scheme will serve roughly to illustrate the behaviour of a paraffin cracked at the lowest possible temperature.



The effects of a rise in temperature on the primary products must now be considerable. The acetylene theory of Berthelot, although it has been widely accepted in the past as the most likely explanation of the formation of aromatic hydrocarbons, appears, in the light of Bone's work, to play only a subsidiary part, as indeed Armstrong and Miller contended in 1886. Assuming that the primary products are paraffin and olefine, it is necessary to trace out the ultimate fate of each. Obviously, given a sufficiently high temperature, both will come into the sphere of reaction. The paraffin will split into still simpler paraffins and olefines, therefore the behaviour of olefines only needs to be considered. At some point or other, ethylene will be encountered as the ultimate olefine. Methylene itself may have a transitory existence. Ethylene gives rise to acetylene as a main product at temperatures averaging 570°–580°. At higher temperatures ethylene is progressively more and more unstaple. The acetylene produced will at once either polymerize or be reduced by free hydrogen to ethylene and ethane. It thus appears that the rôle of acetylene is insignificant. How then is the occurrence of aromatic hydrocarbons to be explained?

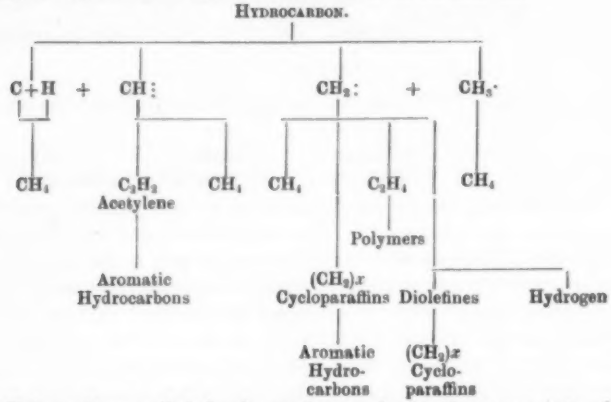
In the first place, the theory of the transitory existence of nascent radicles becomes increasingly important as the cracking temperature rises.

The following scheme (p. 86) shows some of the possibilities.

In the presence of an appropriate catalyst, reduced nickel in particular, Sabatier considers that the molecular scission into nascent radicles goes on at much lower temperatures, such as 350°. If hydrogen be present in excess, then these molecular fragments will tend to be reduced, and consequently paraffin will be produced. On the other hand, at higher temperatures, and in the absence of hydrogen, he finds that carbon and hydrogen are the end-products. Even the more stable cyclic hydrocarbons behave in a similar manner, benzene as an example mainly being degraded to methane.

Now it has been pointed out that the rôle of the catalyst is not to initiate a reaction, but to hasten the final equilibrium, and hence

what happens at a low temperature with the aid of reduced nickel may well proceed at higher temperatures in its absence.



Yet another well-defined reaction undoubtedly comes into play in pyrosynthesis, more particularly at high temperatures, and that is the condensation of two or more molecules, with accompanying elimination of hydrogen, thus :—

$$5C_2H_2 = C_{10}H_8 + H_2$$
naphthalene

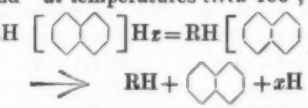
(This equation probably represents only the summation of several consecutive reactions.)

$$2C_7H_8 = C_{14}H_{10} + 3H_2$$
toluene anthracene or phenanthrene

$$2C_6H_6 = C_{12}H_{10} + H_2$$
benzene diphenyl.

This point is borne out by the experiments of Jones and Wheeler [103a], who assume in coal the existence of hydrogenated aromatic nuclei, such as

This " compound " at temperatures *circa* 400°, loses hydrogen :—



In point of fact at this temperature dihydronaphthalene does lose hydrogen.

An interesting side issue is that Jones and Wheeler isolated heptacosane $C_{27}H_{56}$ in coal substance, so that from this standpoint the destructive distillation of coal for coal-gas is a cracking operation.

A final point on the mechanism of cracking may here be emphasized. Starting on the one hand with acetylene at a moderate temperature, and using reduced nickel, Sabatier has synthesized fair imitations of American, Caucasian and Galician oils. On the other hand, by employing higher temperatures, a number of chemists have obtained from the same gas, compounds identical with those occurring in coal tar and of the highest complexity. Does it not appear that the nature of the material to be cracked has little influence on the final products? Taking a concrete case, naphthalene has been identified from the following sources:—

Source.	Observer.
C_2H_2	Berthelot, Meyer & Fricke, Bone & Coward
C_6H_6	Berthelot
Oil gas tar	Armstrong & Miller
Cracked paraffin oil ...	Prunier
„ turpentine ...	Tocher
C_2H_4	Lewes, Bone & Coward, Norton & Noyes
Oil gas tar	Noyes & Mory
Cracked petroleum residues	Engler
„ „ ...	Rittman
„ Baku petroleum...	Letny
„ „ ostatki ...	Redwood
C_2H_6	Bone & Coward
$C_2H_2+H_2$	Meyer & Tanzen
Isoprene	Staudinger
Cracked lignite oils ...	Salzmann & Wichelhaus
„ coal tar oils and petroleum	Liebermann & Burg
Any paraffin hydrocarbons	Worstall & Burwell

The Chemical Nature of the Products from Cracked Oils.—As has been indicated in the preceding pages, cracked oil will contain paraffins, cycloparaffins, olefines, diolefines and aromatic hydrocarbons, the relative amounts of these depending on the experimental conditions under which the oil has been cracked. A detailed investigation of the products obtained under varying conditions is in progress by Mr. Lomax and ourselves, but some of the preliminary results obtained may be briefly mentioned.

Gaseous Products.—The gas produced by cracking oil contains hydrogen, gaseous paraffins, olefines, and diolefines, together with

small amounts of the vapours of volatile liquid products. Mr. Lomax has examined the gas produced by a comparatively low temperature process, cooled by passage through tubes surrounded by ice and salt, then through solar oil cooled by the same means, and finally passed into cooled bromine. The unsaturated components of the gas were absorbed with avidity, and the resulting bromides submitted to fractional distillation in a vacuum. A liquid fraction of comparatively low boiling-point was obtained which, on redistillation at ordinary pressure, was found to consist mainly of ethylene dibromide mixed with smaller amounts of propylene and butylene dibromides. A well-defined portion of high boiling-point was also obtained, which solidified on cooling, and on recrystallization from alcohol gave white leaflets melting at 114° C., whose analytical figures corresponded with the formula $C_4H_8Br_4$ indicating the presence of erythrene.

Liquid Products.—The liquid products obtained by cracking oil are usually produced with one of two objects: either as a source of motor-spirit, or as a source of aromatic hydrocarbons such as benzol and toluol. In the first case the cracked oil is distilled at a suitable temperature, the entire distillate being used as motor-spirit after suitable refining. In the second case suitable fractionation is employed in order to obtain (a) a light motor-spirit nearly free from aromatic hydrocarbons; (b) an "aromatic fraction" boiling approximately between 70° and 170° C., and therefore consisting largely of benzol, toluol and solvent naphtha, and (c) a heavy residue containing no hydrocarbons which it would be worth while to isolate.

The distillate in either of these cases is conveniently referred to as "cracked spirit," and its composition varies in the proportion though not in the nature of its constituents.

The properties of a cracked spirit are familiar to most of the members of this Institution. The spirit is usually yellow, the colour developing on keeping, and the odour most characteristic, resembling somewhat that of coal-gas (since this consists partly of water-gas carburetted by cracked oil). The large proportion of olefines and diolefines present render difficult the refining of the spirit by sulphuric acid, since these combine with approximately their own weight of acid, great heat and discoloration also resulting. As the pronounced odour of the spirit is the intrinsic odour of the mono- and di-olefines (especially of the latter), a product as sweet-smelling as natural petrol cannot be obtained without complete removal of these substances. Apart from the odour, the diolefines possess the curious and, from the motor-spirit point

of view, highly undesirable property of yielding in storage a viscous yellow liquid which is sparingly soluble in the light spirit, and partly separates as a heavy oil. On heating, this thick oil decomposes with almost explosive violence, yielding a hard resinous residue. The supernatant spirit also produces an explosion when distilled, owing to the decomposition of this oil. It is uncertain at present whether this viscous oil is a polymeride or an ozonide derived from the diolefine; it is probably a mixture of several substances of different chemical natures.

The diolefines appear to be produced to a greater extent in cracked spirits made at a fairly high temperature than in those obtained by low-temperature cracking, and moreover predominate in the low-boiling fractions of the cracked oil. Fractions rich in diolefines are converted almost entirely on keeping into explosive resinous products. The lower boiling fractions of cracked spirit are polymerized with evolution of heat by sulphuric and hydrochloric acids and by anhydrous aluminium and ferric chlorides, products of a terpene-like odour and character being produced. Sodium also induces slow polymerization to an oil of high boiling-point and not unpleasant odour.

Several cracked spirits have been fractionally distilled, and the fractions boiling up to 80° shaken with bromine water till this was no longer decolorised. The bromine derivatives have been purified by distillation and analysed, and prove the presence of erythrene, amylene, hexylene, and heptylene.

The portion of a cracked spirit boiling between 70° and 170° always contains benzol, toluol, and xylol. After removal of olefines and diolefines by means of sulphuric acid, these hydrocarbons can be isolated in the form of nitro-derivatives.

The composition of a cracked spirit can be most readily determined by shaking a known volume with excess of cold concentrated sulphuric acid which dissolves olefines and diolefines. If the proportion of diolefines is considerable, the violence of the action may be moderated by shaking first with 80 % acid, which removes most of the diolefines, but only a small part of the olefines. The residue, after measuring, is then shaken with cold, slightly fuming sulphuric acid till no further absorption results. The operations are conveniently carried out in a stoppered burette, and the two absorptions indicate olefines (with diolefines) and aromatic hydrocarbons respectively. The residual spirit is a mixture of paraffins and cycloparaffins. If fractions of fairly definite boiling-point are so analysed, the nature of the paraffins in this residue will be known, and a specific gravity determination will thus indicate the relative

proportions of paraffin and cycloparaffin. A few series of such analyses may be of interest.

A. Fraction (boiling-point, 80°–138°) of "cracked spirit" intended as a source of benzol and toluol.

Loss to Concentrated Sulphuric Acid = 17 % Olefines and Diolefines.
„ Fuming „ „ = 83 % Aromatic hydrocarbons.
Residue ... ... = 0 % Paraffins and Cycloparaffins.

B. Fraction (boiling-point 85°-87°) of "cracked spirit" for motor fuel.

Loss to Concentrated Sulphuric Acid = 46·5 % Olefines and Diolefines.
„ Fuming „ „ = 29·5 % Aromatic hydrocarbons.
Residue ... ... = 24·0 % Paraffins and Cycloparaffins.

C. "Cracked spirit" for motor fuel.

Loss to Concentrated Sulphuric Acid = 18 % Olefines and Diolefines.
„ Fuming „ „ = 7 % Aromatic hydrocarbons.
Residue ... ... = 75 % Paraffins and Cycloparaffins.

Under existing conditions, the bibliography of pyrogenesis, whilst too extensive for publication with full titles, &c., in these pages, is so important and essential to the foregoing text, that we have as a compromise reduced it to the subjoined index of the literature of the subject.

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(The last three on Rittman Process.)

Observer.	Material.	Temperature.	Pressure.	Catalyst.	Products.	Remarks.
Dalton	ethylene	v. high	not stated	none	$C + CH_4$	—
Marchand	,,	bright red heat	,,	,,	$C + CH_4$	—
Buff and Hofmann	,,	dull red	,,	,,	$C + CH_4$	—
Magnus	,,	not stated	,,	,,	liquid products	—
De Wilde	,,	electric sparks		,,	$C_2H_2 + H_2$	questionable.
Berthelot	acetylene	dull red	,,	,,	C_2H_2, C_2H_4, C_2H_6	—
,,	,,	,,	,,	,,	styrolene	—
,,	,,	,,	,,	coke	free hydrogen almost entirely	at higher temp. CH_4 would be formed.
,,	,,	,,	,,	iron	H_2, C_2H_2, and tar	—
,,	acetylene + hydrogen and other diluents	,,	,,	none	slower decomposition	—
,,	acetylene + hydrogen	,,	,,	,,	ethylene	reversible reaction.
,,	styrolene	,,	,,	,,	C_2H_2, C, H_2 and tar with naphthalene	—
,,	ethylene	not stated	,,	,,	C_2H_6, C_2H_2 and tar	evidently reversible.
,,	ethane	,,	,,	,,	C_2H_4	
,,	ethylene + hydrogen	dull red	,,	,,	C_2H_6	equilibrium set up.
,,	acetylene + ethylene	,,	,,	,,	C_4H_6 (divinyl)	60 % yield.
,,	acetylene + benzene	,,	,,	,,	H_2, C_2H_4, C_2H_6 and naphthalene	only 2 % of original gas remained.
,,	acetylene + naphthalene	,,	,,	,,	H_2, C_2H_4, C_2H_6 and naphthalene	
,,	benzene	bright red	,,	,,	diphenyl + H_2, chrysene and resin, no naphthalene or anthracene	—
,,	toluene	,,	,,	,,	C_6H_6, C_7H_8, naphthalene and possibly chrysene	—

Observer.	Material.	Temperature.	Pressure.	Catalyst.	Products.	Remarks
Berthelot	benzene + ethylene	bright red	not stated	none	styrolene, anthracene and naphthalene	—
,,	styrolene	,,	,,	,,	$C_6H_6 + C_2H_2$	—
,,	styrolene + hydrogen	,,	,,	,,	$C_6H_6 + C_2H_4$	—
,,	styrolene + ethylene	,,	,,	,,	C_6H_6 + naphthalene	—
,,	styrolene + benzene	,,	,,	,,	anthracene, naphthalene and diphenyl	—
,,	benzene + naphthalene	,,	,,	,,	anthracene + hydrogen	—
,,	anthracene	,,	,,	,,	benzene and chrysene	—
,,	toluene	,,	,,	,,	benzene, toluene (5%), naphthalene, dibenzyl, anthracene and chrysene	1 gram per minute through 35 cm. porcelain tube.
,,	xylene	,,	,,	,,	chiefly toluene, benzene, xylene, naphthalene and anthracene	—
,,	cumene	,,	,,	,,	benzene (small amount), toluene, xylene, cumene, naphthalene, anthracene and chrysene	—
Faraday	liquid from compressed oil gas	,,	,,	,,	chiefly benzene	—
Armstrong and Miller	,,	,,	,,	,,	divinyl, olefines, acetylenes, benzene, 'hexoylene' (hexine C_6H_{10}). no paraffins	—

				no paraffins		
Armstrong and Miller	tar and liquid due to compression of gas from above experiment	bright red	not stated	none	polymerizable hydrocarbons, benzenes, toluene, xylene, mesitylene, pseudo-cumene and naphthalene, crotonylene, olefines up to *n*-heptylene. Traces of paraffins and naphthalene	—
Thorpe and Young	repeated distillation of paraffin wax (44·5 M.P.)	B.P. of the wax	15-30 lbs.	,,	olefines and small amount of paraffins, in fractions up to 100°, no benzene 100°-200° fraction gave olefines and paraffins to nonene and nonylene	implest cases of cracking. No carbon or hydrogen set free.
Prunier	paraffin oils	"strong heat"	not stated	,	C_2H_2, C_4H_6, C_5H_{10}, C_6H_{10}, and C_6H_6, styrolene, naphthalene	degree of saturation of products varies with temperature, pressure and time.
Greville Williams	heavy petroleum	bright red	,,	,	aromatic hydrocarbons	products in oil from compressed Pintsch gas.
Pring and Hutton	carbon and hydrogen	1850°	,,		CH_4 and C_2H_2	acetylene denied by Bone.
Pring	,,	1100° 1550°	,,	,,	Proportion of methane rises. Acetylene decomposes to ethylene and methane	—
Tocher	paraffin oils	500°-600°	,,	,,	C_2H_4, CH_4, H_2 and olefines	—
,,	turpentine	800°	,,	,,	aromatic hydrocarbons and tar	—

Observer.	Material.	Temperature.	Pressure.	Catalyst.	Products.	Remarks.
Lewes	ethylene	800°–900°	not stated	none	CH_4 and C_2H_2 which polymerized to C_6H_6	*See* Bone and Coward.
,,	,,	1000°	,,	,,	naphthalene	—
,,	,,	1100°	,,	,,	C_2H_2 and C and H_2 by decomposition of naphthalene	—
,,	,,	900°	,,	,,	$H_2 + C_2H_4$	*See* Bone and Coward.
,,	Russian oil	oil gas making	,,	,,	aromatic hydrocarbons in the tar and possibly hexane and hexylene, heptane and heptylene and nonane	—
Noyes, Blinks & Mory	oil gas	750°–1,000°	,,	,,	C_4H_6, C_2H_4 and propylene in gas: aromatics (chiefly naphthalene, also anthracene and chrysene) in tar	—
Ipatiev	ethylene	400°–450°	,,	iron and copper	polymers	—
,,	,,	high temperature	—	,,	C_2H_6, CH_4, H_2 and polymers	tends to an equilibrium.
,,	$C_2H_4 + H_2$ (excess)	,,	—	,,	CH_4 and polymers	—
,,	$C_2H_4 + H_2$ (excess)	,,	—	nickel powder	CH_4, C_2H_6	dp/dt varies between 400° and 450° C.
,,	$C_6H_6 + H_2$	400°–450°	220 atmosph.	iron, copper or alum'um	product contains no cyclohexane	—
,,	,,	,,	,,	nickel	cyclohexane (quantitative yield)	reversibility.
,,	cyclohexane	,,	150 atmosph.	none	C_6H_6, H_2, paraffins and olefines	

Engler and Lehmann	fish oil	distilled under pressure	150 atmosph.	none	solid paraffin, M.Pt. 49°–51°, olefines, benzene and its homologues; no naphthenes proved	—
Engler	animal fats	,,	,,	,,	light hydrocarbons which polymerize into heavier bodies	—
,,	residues from petroleum B.P. + 200	,,	with or without pressure	,,	olefines, naphthenes and aromatic hydrocarbons, whilst the residue becomes poorer in hydrogen	—
Engler and Grüning	petroleum	cracked for burning oils	—	,,	olefines and paraffins from C_3 to C_{10}, benzene and its homologues	—
Engler and Schneider	,,	distilled	6 atmosph.	,,	similar results to above	
Ipatiev	ethylene	380°–400°	70 atmosph.	,,	below 250° C. rapid polymerization to paraffins, olefines and cycloparaffins: above 250° there is formed a range of bodies poorer in hydrogen. Ipatiev isolated paraffin from pentane to nonane, amylene and hexylene, cycloparaffin from C_5 to C_{15}	olefines are probably produced by polymerization of ethylene or scission of polymethylene rings, paraffins by hydrogenation of cyclic compounds, or by fission of side-chain from polymethylene nucleus.
,,	isobutylen	,,	,,	,,	aromatic hydrocarbon	—
,,	ethylene	,,	,,	Al_2O_3	better yield of aromatic hydrocarbons	—
,,	,,	600°	atmosph.	none	does not polymerize	—

Observer.	Material.	Temperature.	Pressure.	Catalyst.	Products.	Remarks.
Ostromislenski	dipentene	400°–600°	atmospheric	none	isoprene (dimethyl erythrene)	depolymerization.
,,	open chain hydrocarbons	,,	,,	,,	erythrene (divinyl) and 1·3 butadiene	—
,,	Russian crude petroleum	600°–700°	,,	nickel	coke and gas (entirely saturated)	—
,,	naphtha	—	,,	iron	C_2H_2 which polymerizes to benzene	—
Meyer and Fricke	acetylene	not stated	,,	none	*m*- and *p*-xylene, α and β methyl naphthalene and reduced naphthalenes in the tar. 23 compounds which are present in this tar are present in ordinary coal tar	—
Whitaker and Alexander	kerosene (150°–290° B.P.)	1,600°	,,	,,	gas contained 96% H_2 at feed of 30 cc. per minute. Carbon and H_2 only at feed of 10 cc. per minute	—
,,	,,	800°	,,	,,	gas contained 52% illuminants	—
Brooks	Texas solar oil (sp. gr. ·8862)	400°–600°	,,	various contact substances	3% to 20% yield of highly unsaturated gasoline (28% absorbed by sulphuric acid)	—
,,	Oklahoma reduced oil (sp. gr. ·875)	not stated	450 lbs.	none	yield of gasoline increased with pressure up to 250 lbs. and then decreased. Unsaturation decreased as pressure increased up to 250 lbs.	production of aromatic hydrocarbons is ascribed to the fission of high-boiling phenylated compounds and not to polymerization of acetylene.

Rittman and Egloff	middle tar oils	not stated	not stated	none	yield of benzene and toluene depends on the proportion of the oil cooling below 200°. The heavier oils are unsuitable for cracking	—
Brooks and Humphrey	Jennings and Oklahoma oil B.P. above 275°	420°	100 lbs.	,,	small amounts of benzene and toluene and *m*-xylene	—
,,	,,	not stated	not stated	aluminium chloride	,, ,, ,,	heavy petroleum contains phenylated compounds causing *e.g.* fluorescence.
,,	paraffin wax	,,	,,	none	no aromatic hydrocarbons	—
,,	synthetic "phenyl paraffin"	,,	,,	aluminium chloride	benzene and toluene	—
Davies	high boiling petroleum mixed with superheated steam	650°–675°	100 lbs.	iron shavings	gasoline almost free from unsaturated compounds	—
Egloff & Twomey	paraffin wax, M.P. 47	500°	atmospheric	not stated	no aromatic hydrocarbons	Rittman plant.
,,	,,	600°	,,	,,	aromatic hydrocarbons	—
,,	,,	500°–600°	150 lbs.	,,	,, ,,	—
Egloff	neutral tar oil, 150°–325°	650°	14 atmosph.	,,	3·2 % benzene	causes for benzene and toluene formation: (1) direct decomposition of methyl naphthalene. (2) formation and decomposition of xylene. (3) polymerization of acetylene and methylacetylene.
		600°	14 ,,	,,	2 % toluene	
		650°	11 ,,	,,		
,,	petroleum	600°–700°	atmospheric	,,	degree of unsaturation increased to 700° and then declined	
Egloff & Twomey	gas oil	450°–600°	,,	,,	benzene, toluene and xylene	—

Observer.	Material.	Temperature.	Pressure.	Catalyst.	Products.	Remarks.
Egloff & Twomey	gas oil	750°	atmospheric	not stated	naphthalene	—
,,		800°	,,	,,	anthracene	—
Whitaker and Leslie	kerosene mixed with hydrogen	621°	,,	,,	absorption of H_2 is greater as the temperature and concentration increases: methane is formed more readily at higher temperatures	—
,,	,,	723°	,,	,,	—	—
,,	,,	825°	,,	,,	—	—
Anschütz	—	—	—	—	—	formation of complex hydrocarbons is due to condensation and elimination of H_2
Ipatiev and Dowgelewitsch	hexane	650°–700°	atmospheric	alumina	paraffins, olefines and hydrogen; no aromatics	—
—	,,	,,	high pressure	,,	explosion occurs	—
—	cyclo-hexane	500°	,,	,,	olefines, cyclo-paraffins and benzene	—
Norton and Andrews	*n*-hexane	bright red	not stated	not stated	olefines to hexylene, benzene and butin: small amount of paraffins	—
,,	,,	550°	,,	,,	no action	—
,,	,,	600°	,,	,,	no gas; traces of unsaturated bodies	—
,,	,,	700°	,,		olefines to hexylene; butin small; no benzene	—
,,	*iso*-hexane	bright red	,,	,,	olefines to hexylene and butin	—

Norton and Andrews	*n*-pentane	bright red	not stated	not stated	ethylene, propylene and erythrene	—
Day	ethylene	350°	,,	,,	trace of decomposition	—
,,	,,	400°	,,	,,	methane, ethane and liquid products	
Letny	residues from Baku petroleum	red heat	,,	wood charcoal	benzene and homologues, naphthalene, phenanthrene and anthracene	—
Gustavson	American ligroin, Caucasian kerosene	1,200°	,,	aluminium bromide	methane and simple olefines	—
Lisenko	residues from petroleum	434°–501°	,,	not stated	increased yield of kerosene	—
Engler and Rosner	Baku crude oil gas	not stated	,,	,,	mainly olefines, hydrogen, methane and ethane	—
Nikiforoff	double cracking of heavy oil (Baku)	525°–550° 700°-1,200°	atmospheric 2 atmospheres	,, ,,	12% yield of crude benzol	Ogloblin by same methods obtained 5·6% benzene, 4% toluene, 2·1% xylene.
Zelinski	cyclo-hexane	170°	not stated	palladium	begins to decompose	active.
,,	,,	200°–300°	,,	,,	benzene and hydrogen	reversible at 100°–110°.
,,	methyl cyclo-hexane	,,	,,	,,	toluene and hydrogen; no trace of di- or tetra-hydro-derivatives of cyclo-hexane	no reaction with the cyclo-pentane derivatives below 300°.
,,	cyclo-hexene (ex cyclo-hexanol)	,,	,,	,,	benzene and hydrogen	—
,,	cyclo-hexene (ex iodo cyclo-hexane)	,,	,,	,,	benzene and a new cyclo-hexene	—

Observer.	Material.	Temperature.	Pressure.	Catalyst.	Products.	Remarks.
Zelinski and Herzenstein	cyclo-hexane and methyl cyclo-pentane	300°	not stated	palladium	H_2, benzene and unchanged methyl cyclo-pentane	illustration of the stability of the cyclo-pentane ring.
,,	Baku naphtha (102°–104°)	,,	,,	,,	toluene and methyl cyclo-hexane, probably cyclo-pentane derivative	—
Dobrochotov	Baku naphtha (103°–105°)	,,	,,	,,	toluene and product similar to starting material of previous experiment by Herzenstein	—
Jones	cyclo-hexane	495°–500°	atmospheric	porous porcelain	hydrogen, methane, ethane, olefines, benzene	—
,,	methyl cyclo-hexane	500°–510°	,,	,,	begins to decompose	—
		530°			similar products to that from cyclo-hexane	—
,,	1–4 di-hydro-naphthalene	420°	,,	,,	hydrogen, methane, naphthalene and traces of olefines	—
,,	1, 2, 3, 4, tetra-hydro-naphthalene	530°	,,	,,	hydrogen, methane, ethane, ethylene, benzene, and naphthalene	—
Boissieu	mazout	dry distillation	not stated	—	10–12 % aromatic hydrocarbons	—
Dvorkovitz	oil vapours from heavy oil	704°–871°	,,	hot iron plates	aromatic hydrocarbons	—
Edeleanu	superheated petroleum	not stated	,,	not stated	aromatic hydrocarbons	—
Pamphilov	petroleum vapour	dull red	—	—	15 % benzene in the tar	—
Redwood	ostatki	Nobel's regenerative furnace	not stated	not stated	benzene, anthracene and naphthalene	—

Veith	residues	700°–800°	—	—	aromatic hydrocarbons	yield depends on temperature and rate of feed.
Bone & Coward	methane	1000°	atmospheric	not stated	carbon, hydrogen, and methane (trace of acetylene at early stages)	—
,,	—	700°	,,	,,	no decomposition unless catalyst present	entirely surface decomposition.
,,	—	785°	,,	,,	carbon hydrogen and methane	—
,,	—	1150°	,,	,,	carbon, hydrogen and methane	—
,,	ethane	675°	,,	,,	acetylene, ethylene, and ethane in small quantities, mainly methane, carbon, hydrogen and trace of naphthalene	—
,,	—	800°	,,	—	CH_4, C and H_2 (traces of C_2H_4, C_2H_2 and aromatics at early stages)	—
,,	—	1000°	,,	—	CH_4, C and H_2 (traces of C_2H_2. At early stages C_2H_2, C_2H_4 and C_2H_6	—
,,	—	1140°–1185°	,,	—	CH_4, C and H_2 (at early stages trace of C_2H_2)	—
,,	ethylene	570°–580°	,,	—	C_2H_2, C_2H_6, CH_4 and H_2, little aromatic hydrocarbons and C	—
,,	—	700°–720°	,,	—	less C_2H_2, main products are C_2H_6, CH_4, H_2	—
,,	—	800°	,,	—	main products CH_4, C, H_2, traces of C_2H_2 (at early stages C_2H_4 and C_2H_2)	—
,,	—	950°	,,	—	CH_4, C and H_2 (at early stages C_2H_4 and C_2H_2)	—

Observer.	Material.	Temperature.	Pressure.	Catalyst.	Products.	Remarks.
Bone & Coward	—	1180°	atmospheric	—	mainly C and H_2 and little CH_4 (at early stages C_2H_2 and C_2H_4)	—
,,	acetylene	480°–500°	,,	porous porcelain	C_2H_2, C_2H_4, C_2H_6, C & H_2 and aromatic hydrocarbons, main products were polymerized	—
,,	,,	650°	,,	,,	50 % polymerized 30 % carbon & hydrogen 10 % C_2H_2, C_2H_4, CH_4	—
,,	,,	800	,,	not stated	final product C, C_2H_6 and CH_4 (at early stages C_2H_4 and C_2H_2)	—
,,	,,	1000°	,,	,,	CH_4, H_2 and C (at early stages C_2H_4 and C_2H_2)	—
,,	,,	1120°–1150°	,,	,,	C and H_2, trace of CH_4 (at early stages C_2H_4 and C_2H_2)	—
McKee	benzene	700°	,,	,,	begins to decompose	—
Meyer and Tanzen	acetylene and hydrogen	640°–600° 800°	—	—	*n*-hexylene and aromatic tar obtained, containing phenanthrene, acenaphthenes and styrolene	—
Routala	amylene	heat under pressure	—	not stated	naphthenes	—
Aschan	olefine	low temperature	not stated	aluminium chloride	polymerization to cycloparaffins	—
Ipatiev and Routala	C_2H_4	275° C.	70 atmosph.	zinc chloride	polymerization	naphthenes.
,,	—	—	—	aluminium chloride	polymerization at lower temperatures	increase with temperature.

Kuznetzov	CH_4 C_2H_2 C_2H_4 C_2H_6	660°	—	aluminium	decomposition to elements	same result by Lidov and Kuznetzov, using magnesium.
Smith and Lewcock	benzene	795°	atmospheric	carbon deposited acts as catalyst	53 % yield of diphenyl; also carbon and hydrogen	condensation with elimination of hydrogen.
Worstall and Burwell	*n*-heptane *n*-octane	900° in Pintsch gas retorts	not stated	not stated	coke, tar (25 %), spirit (10 %) and gas; methane, heptane, octane and ethylene; no acetylene or naphthene, benzene and its homologues; naphthalene, anthracene, phenanthrene and chrysene	these products are precisely similar to those found in coal-gas and coal-tar.
Haber	*n*-hexane	600°–800°	,,		amylene and methane	this type of decomposition appears to be a general reaction in the first stage of pyrogenesis.
,,	benzene	not stated	,,		tends to form diphenyl and hydrogen	greater stability of the ring compound.
,,	*n*-hexane	900°–1000°	,,	,,	coke, tar, hydrogen, methane, ethylene and aromatic hydrocarbons	the formation of benzene from hexane is not direct.
Friedmann	*n*-octane	280°	under pressure	,,	slight production of lower-boiling products	the higher the molecular weight of a paraffin, the more easily it decomposes.
Zanetti	propane (97 %), butane (3 %) mixture	750°	atmospheric	,,	olefines and hydrogen; no aromatic hydrocarbons; unsaturated hydrocarbons are at a maximum	—

Observer.	Material.	Temperature.	Pressure.	Catalyst.	Products.	Remarks
Zanetti	propane (97 %), butane (3 %) mixture	above 750°	atmospheric	not stated	benzene and toluene are produced	—
,,	,,	,,	,,	nickel and iron	these catalysts inhibit the formation of aromatics and promote decomposition to carbon and hydrogen	—
Zelinski	—	—	—	—	—	alumina and titanic oxide promote the formation of aromatic hydrocarbons.
Tchitchibabin	acetylene	not stated	not stated	various	(*a*) local decomposition to carbonhydrogen (*b*) polymerization to benzene (*c*) condensation to solid hydrocarbons (*d*) hydrogenation to paraffins, olefines and naphthenes	—
Jackson and Lawrie	,,	high frequency discharge	,,	not stated	a solid polymer $(C_2H_2)_x$, which on heating produces methane and liquid hydrocarbons	—
Sernagiotto	—	—	—	—	transitory existence of $:CH_2$ radicle shown by formation of $(CH_2)_x$ cyclic and unsaturated hydrocarbons by action of phosphoric oxide on methyl alcohol	—

Staudinger	isoprene	400°	not stated	not stated	a little amylene and terpenes	—
,,	,,	600°–700°	—	—	unsaturated hydrocarbons	—
,,	,,	700°–750°	—	—	aromatics in small amount	—
,,	,,	800°	—	—	aromatics only	—
Engler	amylene	not stated	not stated	not stated	methane and hydrogen	—
,,	,,	atmospheric	,,	aluminium chloride	" lubricating oil "	—
Rittman and Twomey	gas oil	not stated	,,	not stated	benzene formation needs rigorous cracking. Toluene and xylene both yield benzene. Naphthalene is formed by the cracking of monocyclic aromatic hydrocarbons	—
Slater	methane	,,	,,	various surface agents — lime, charcoal, graphite, iron, carborundum, etc.	all increase velocity of decomposition	reverse action i found by Ipatiev to be accelerated by presence of metallic oxides.
,,	—	—	—	silica	the action is retarded	—
Rittman, Byron and Egloff	—	—	—	—	progress of formation of aromatic hydrocarbons is in this order—cymene → xylene → toluene → benzene → naphthalene → anthracene → carbon and gas	irreversible.

Observer.	Material.	Temperature.	Pressure.	Catalyst.	Products.	Remarks.
Rather and Reid	ethylene	180°	atmospheric	nickel or kieselguhr	ethane	—
Gurvitch	amylene	atmospheric	,,	floridin, alumina and carbon	mainly diamylene	—
Losanitsch	isopentane	silent electric discharge	*in vacuo*	—	hexa-methyl cyclo-butane and dimethyl octane	results which hitherto were only obtainable with high temperature and pressure are here brought about by cold electric discharge.
,,	olefines and aromatic hydrocarbons	,,	,,	—	rapid polymerization	
Egloff & Moore	kerosene	not stated	not stated	—	various elements in presence of HCl	best results of gasolene from $AlCl_3$
					various elements in presence of chlorine	best results with $AlCl_3$
Montmollin	alcohol and phosphoric acid	280°	atmospheric	—	products solated were synthetic hydrocarbons, paraffins, polymethylenes and olefines	—
F. Fischer	naphthalene	330°	sealed tube	$AlCl_3$	40 % converted into oil containing reduced naphthalenes	—
Liebermann & Burg	coal tar oils and petroleum	red hot	atmospheric	coke	aromatic hydrocarbons	—
Salzmann & Wichelhaus	lignite oils	,,	,,	pumice, charcoal and platinised asbestos	aromatic hydrocarbons	—

DISCUSSION.

Sir Boverton Redwood said that, in view of the amount of attention devoted at the present time to the subject, it would be safe to predict that a large number of investigators would owe a deep debt of gratitude to the talented and industrious authors of the paper to which the members had just listened. Further, it might be said that the Institution of Petroleum Technologists had taken important action, entitling it to credit, by arranging for the placing on record of so comprehensive an account of the evolution of the process of cracking, and of the principles underlying it. The subject was, all would agree, one of entrancing interest, as well as of great industrial importance, and he thought that a careful study of the paper might lead to further developments of an entirely unsuspected nature. This paper would therefore form a most valuable permanent record of an authoritative character for future study. The speaker was precluded from discussing the relative merits of the process with which his name was associated and of other methods of achieving the same results. He thought also, that as a measure of precaution he ought to disclaim acquiescence even in the views of the authors on that particular point, however much he might or might not agree with them. At any rate he could safely say that his old friend, Professor Dewar, and himself had been born too soon. No one was in a better position than Mr. Lomax and his associates authoritatively to speak of the results obtained by the working of the Hall process "somewhere in England," for a period of nearly a year, on a practical scale, for the manufacture of toluene. He would, however, like to add his own personal testimony to what had been so well said as to the efficiency of that method of obtaining aromatic hydrocarbons from petroleum. Although the inventor of the process was an American citizen, a subject of the United States, the speaker nevertheless felt proud that his process was practically worked out and brought to a success in this country; and that it was being most successfully worked, and was giving admirable results at a time when, according to published statements, the workers at the Rittman process, under the aegis of the United States Bureau of Mines, were still grappling with difficulties which in this country had been encountered at an earlier stage, and had already been successfully overcome.

Dr. M. B. Blackler said that a monumental work had been produced by the authors on a subject which, to his mind, would become of great economic importance in the near future. Cracking

could be considered from two points of view, (1) the production of aromatic hydrocarbons, and (2) the production of motor fuel for internal-combustion engines. He did not believe that when aromatic hydrocarbons became the servants of peace, the production of these bodies from petroleum by the cracking process would have an economic value, but he was certain that this process was going to be of great assistance in the production of fuel for the future requirements of the high-speed internal-combustion engine. In a process of this description, where molecules of a complex nature were subjected to high pressure, and passed through heated tubes at the velocity of an express train, it was necessary to choose conditions which offered the maximum results for the purpose in view, namely to produce a spirit which could be placed on the market at an economic price. So far as the speaker's experience carried him, he could agree with Dr. Dunstan's view that in the action described the heavier hydrocarbons were broken down mainly into three distinct classes—paraffins, olefines, diolefines, with smaller quantities of aromatic hydrocarbons and heterocyclic hydrocarbons, and varying quantities of gas. From the economic point of view it was the diolefines which affected the utility of the fuels produced. Crude cracked spirits possessed an atrocious odour, and in a longer or shorter time, deposited heavy material of a gummy consistency, which was detrimental to its use in the ordinary carburetter. Before placing cracked spirits on the market, it would therefore be necessary to develop a process which would economically eliminate the diolefines, which were prone to polymerization, while still leaving the whole of the olefines present in the crude spirit. The usual method of purification was to use some strong chemical, like sulphuric acid, which acted not only on the diolefines but on the olefines also, and it was impossible to restrain it in such a way that it would act on the diolefines only. In addition to the unnecessary loss caused by this method of purification, a certain residuum of diolefines was always left behind, which changed after the material had been standing some time, and the spirit then deposited "gum," and developed an objectionable odour. It was thought that if some definite chemical or chemicals, not necessarily strong, could be discovered, which would have a selective action on the bodies that were slightly more unsaturated (the diolefines) than on the other unsaturated bodies present (olefines and aromatics), it might be possible to develop a process which would rid the cracked spirit of the undesirable diolefines, and leave behind olefines and saturated bodies which would not undergo change. He was not

in a position to give details, but that process had been worked out, and it had been found that it was possible to eliminate the whole of the diolefines from the crude spirit, leaving behind a colourless, odourless product, containing olefines and paraffins, together with small quantities of aromatic hydrocarbons and polymethylenes; then, no matter how long this product was kept, it would not undergo any change. If, however, the process were not conducted with sufficient care, and small quantities of diolefines remained in the finished product, a change did take place after four or five months standing and there was a gradual deposition of gummy matter, and an objectionable odour developed in the spirit. In a complex process such as that under review, no matter how temperature and pressure were controlled, it was impossible to guarantee that a certain percentage of the obnoxious diolefines would not be obtained, and in the majority of cases six to eight per cent. would be present.

A peculiar property of the spirit obtained by the cracking process, which would in the speaker's opinion, influence the fuel question, was that these spirits, unlike petrol, mixed with alcohol. It had been previously determined that alcohol mixed with a certain quantity of benzene was an excellent fuel for a petrol engine. The speaker felt sure therefore that in the future, when the supply of petrol became insufficient for the world's demand, cracked spirit obtained from heavy hydrocarbons would be mixed with alcohol in proportions up to 50 %, and used as fuel for high-speed internal-combustion engines. An interesting point is the boiling-point of such a mixture. When purified cracked spirit, boiling from 35° C. to 220° C., was mixed with an equal quantity of alcohol, 90 % of the mixture boiled below 100° C.

Dr. F. M. Perkin remarked that the question of cracked spirit was, as Dr. Blackler had stated, one of an economic character entirely. If at the present time oil could be cracked in such a way as to produce hydrocarbons of the benzene series, such as benzol, toluol, etc., this would be better than cracking it in any other way. It was known that when cracking at such very high temperatures as would be necessary caused very much larger quantities of gas to be produced, and there was also the great difficulty of the deposit of carbon. Personally, he was not a believer in the Rittman process, where a chain had to be kept constantly swirling round in order to remove the carbon into receiving pots below, and where the working pressure was something like 150 lbs. In the Hall process, the principle was quite different; there it was a question of expanding into a chamber to get rid of the carbon,

and in that case there was no great difficulty in getting up high temperatures. He had had no experience in trying to crack mineral oils to get the hydrocarbon aromatic series; in fact, he had never attempted to do it. But as the process by Fenchelle and himself had been mentioned, he would say that in that case the conditions of working were such as to give a less proportion of carbon than probably any other process; simply for the reason that the oil, during the whole time that it was passing through the process, was kept in a liquid condition. The pressure upon the oil, no matter what the temperature might be, was always so high that the oil never reached its critical temperature, and never, therefore, passed into the form of vapour. Under these conditions there was, of course, less possibility of complete decomposition into carbon and hydrogen than happened in other cases. He might say, from an experience ranging over about eighteen months, on a fair sized plant, dealing with about 180 gallons per hour, the tubes employed, which were moderately narrow, had only been choked with carbon on two or three occasions, and in these instances largely by trying experiments for which the plant was not intended. For example, an attempt had been made to crack green oil of the gas works, which, of course, contained hydrocarbons of the benzene series, and large quantities of naphthalene and anthracene, which immediately wanted to break up into carbon and other undesired products. In dealing with ordinary fuel oil, containing practically no aromatic hydrocarbons, there was no great difficulty in obtaining petrol. But there arose the same difficulty as obtained in other processes, no matter what the process was: the gummy dienes and trienes and the like were produced. The next problem was, in what proportion were these going to be formed? Was it possible to remove them with 1 % of sulphuric acid, or would it be necessary to add 5 %, 6 % or 10 % to get rid of them? Further, when it was supposed they had been removed, were they going to reform again in about a year's time? That was the difficulty. There might be only 2 % or 3 % of these gum-forming hydrocarbons, which on complete or partial removal gave a beautiful, clean-looking petrol. Frequently, however, if this was stored for a year or eighteen months the "gum" would have formed again. If the hydrocarbons were to be used immediately after their first purification, would the gummy substances actually be there and clog the valves, say in the ascent of a stiff hill, or other critical occasion, or were they only formed again by prolonged storage? As a matter of fact they formed very much more rapidly in sunlight

than in the dark. He thought that the cracked petrol should be used within six weeks of its purification. That had been a difficulty in the case of a good many processes hitherto, and although the speaker, like Dr. Dunstan and his confrères, and Dr. Blackler and Mr. Lucas, had done a large amount of experimental work, the difficulty of keeping out the gummy products had not been overcome, though he was confident that it would be got over in due course. He did not, however, agree that the cracked oils had an unpleasant odour; he rather liked the smell of them. The public had to remember that when they were dealing with cracked oils, they were not dealing with petrol as obtained from the oilfields: it was not the same product; it had a different smell, just as a eau de Cologne varied in smell from oil of lavender. Undoubtedly, in due course the right process would be evolved for purifying these cracked oils, and the work of the authors would go a very long way to forward that achievement. The wonderful bibliography would form a standard in the annals of the Institution of Petroleum Technologists. Dr. Dunstan's equations were of inestimable value. It was only by combination, each student learning from others, and not being afraid to let others know what was being done, that the industry would go ahead.

Mr. A. D. Lucas, who spoke next, had little criticism to offer on what had been said. He could only speak as an engineer, and not as a chemist. The explanation of the processes of cracking had been extremely thorough and complete, and what he had to say related more to the practical side of the question than to the theory. One point in particular occurred to him. Dr. Perkin had referred to the formation of gummy products with time, due, he presumed, to some form of polymerization. Now, a point on which there had been very little literature and very little experimental work was the rate of cooling after the cracking temperature had been reached. The speaker believed that the particular atom of carbon appearing in a final radicle like CH_2 or CH_4, as the case might be, was not in that radicle from the moment it was formed up to the time it was subsequently isolated. Probably it took several forms, at one time CH_2 and at another time CH_4, until it finally settled down. The first time an olefine was formed in the process of cracking from paraffin, it repeatedly broke up and reformed again before it took its final form. If that were so, the rate at which it was cooled after breaking up the original oil, whatever that was, must have a great influence on the final product. He had found by actual experiment that if gases were allowed to remain at a certain temperature for a considerable period, and

cooled slowly, the products were quite different in many respects from those which would be obtained with sudden cooling; in other words, sudden expansion after heating would give totally different results from those obtainable by cooling at the same pressure as the vapour issued from the cracking tube.

In regard to the effect of catalysis, the speaker quite agreed with what the authors had said, and in all probability the term "catalysis" was a convenient one for covering a multitude of sins; in nine cases out of ten the catalyst did not act as a catalyser at all. It might possibly, however, have a selective occlusion effect. A particular catalyst might pick up and hold dissociated vapours, and bring them under such conditions that they re-constituted themselves into more or less saturated or semi-saturated bodies. Having been so formed, these were removed mechanically from the surface, which thus became available for occluding further radicles, which again associated together, and were in turn removed mechanically from the surface of the catalyser. The reason the speaker considered that there must be some such effect as he had described was that he had used a catalyser made in a somewhat peculiar way, mechanically. This catalyser was not in the true sense spongy, but it was mechanically spongy, and had the property of absorbing petrol like cotton wick. It consisted, however, of such hard material that it might be cut with a knife, and show an absolutely metallic section. It was not a catalyser like finely-divided nickel; it was much coarser, but was extremely efficient as a catalyser. Its catalysing properties decreased when it was first used, but after a time they began to rise until they reached the top of the curve where they were most efficient, and from that they descended very slowly and steadily. There was no evidence of deterioration, mechanical or otherwise, but after the catalyser had been in use some time it was found that on heating it certain compounds issued from the catalyser body. He was not sufficient of a chemist to say what those compounds were, but there was distinct evidence of some modification of the nature of the catalyser, and these compounds apparently entered into its reactivities. He had in his laboratory samples of oil-products carefully prepared, in 1912, both by the Lamplough process and the New Oil Company's process: the bottles could be turned upside down, open, and the oil products would not flow out.

Mr. W. J. A. Butterfield wished to add his thanks to those already accorded to the authors, and in particular to Mr. Lomax for the magnificent and invaluable bibliography, in which he could see no omissions, unless at one point, viz., about 1890, when the

American gas engineers and chemists were doing a lot of work on the cracking of oils in connection with carburetted water-gas plant (see the *Progressive Age* and the American *Gaslight Journal* of that period). A. H. Elliott showed as early as 1885 (*Amer. Chem. Journ.*, vi, 248) that carburetted water-gas tar, as then made, was largely composed of aromatic hydrocarbons, since he found 2·6 % to 2·9 % of anthracene in it. At a rather later date, when carburetted water-gas plant was introduced into this country, opportunity was afforded of studying the cracking of heavy oils in that plant. It was easy to work such plant to produce liquid products consisting almost wholly of aromatic hydrocarbons. In "The Chemistry of Gas Manufacture," first published in 1895, he had described a liquid he had examined in 1893 as "a pale clear liquid, obtained by vigorous scrubbing of carburetted water gas after the grosser matters have been deposited in the purifiers and other apparatus. It had a specific gravity of about 0·89, and contained 30 % to 35 % by volume of benzene. This liquid only yielded about 5 % of pitch, but much naphthalene." He thought a valuable lesson might be learnt from some of the earlier experiences with carburetted water-gas plant, in the cracking of oils, for present application in the cracking of them for the production in particular of aromatic hydrocarbons. If the United States authorities, instead of sticking to the advice of the academical staff of the Bureau of Mines, had gone to some of the highly-experienced gas engineers and chemists of the States for an opinion on the Rittman system, a great deal less money would have been wasted on it. In that method of cracking a wide tube was employed, 8 inches in diameter, and there was comparatively little surface-action. Radiation, of course, could have no effect on a real gas, but passing through that tube were particles of liquid in the form of spray, and undoubtedly the radiant heat from the sides of the tube acted on those particles in a totally different manner from the contact heat of a hot substance. A much larger proportion of carbon was produced in cracking liquid particles by radiation in that way. That had been the experience in coal-gas retorts, where the difference in the tarry products between retorts partially and fully filled was very noticeable. In conclusion, he would like to call attention to the question put by the authors towards the close of the paper: "Does it not appear that the nature of the material to be cracked has little influence on the final products." In this connection he congratulated himself that some twenty years ago he had written to the same effect when referring to the composition of the oils deposited from

oil-gas and carburetted water-gas, viz., "The composition of the deposited oils is less dependent on the kind of oil used in the manufacture of the gas than on the heat employed in the production." The authors' work had led them to the same conclusion.

Mr. E. H. Cunningham Craig wished to ask one question. These cracking processes had taken place with the idea of producing either a motor-spirit or the carbon-ring compounds. He would be glad to know what conditions the authors considered most favourable for the formation of the maximum of methane. He presumed that a high temperature would be best, with, probably, very little pressure. It was possible that some people might at some time want to obtain a maximum of methane as pure as possible, whilst not concerned in any way with the formation of motor-spirits, gummy or otherwise, or carbon-ring compounds.

Dr. A. E. Dunstan then replied to the discussion. He had been much interested in hearing Dr. Blackler's account of the effect of alcohol in reducing the boiling-point of cracked spirit mixtures. With regard to gumming, he wondered whether the various speakers on this point would incline to the view that ozonides were produced. The effect of sunlight rather suggested that this was the case, and if so, when the dienes and trienes were removed, further deposits of gummy matter were, as Dr. Blackler had pointed out, unlikely. He had no experience of any case where a simple olefine could be turned into a gummy body by the effect of light and oxygen; it might, of course, be possible, but he was not aware of it. With regard to the separation of diolefines and olefines in the laboratory, with the ordinary reagent, as Dr. Blackler would know, the reactivity of the two classes of compound was not so very different: whatever removed the diolefine would remove the olefine. He could only presume therefore that Dr. Blackler made use of some special method, possibly of the contact action type, which produced the effect. With regard to maximum methane production, the speaker would be inclined to heat the oil to about 1,000° C. in the presence of ample hydrogen.

The President then asked the members to record a very hearty vote of thanks to the authors of the paper. Mr. Lomax had, in a most attractive way, presented a very valuable bibliography, of the greatest utility to everyone interested in the subject, whilst Dr. Dunstan had delivered parts of his paper most fascinatingly, and the illustrations he had furnished proved his mastery of his subject. On behalf of the members, he expressed to the authors how deeply indebted to them the Institution felt.

The vote of thanks was passed by acclamation.